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I. P. Beletskaya on occasion of her jubilee

New Stable Germylenes, Stannylenes, and Related Compounds II.* Bis(butylthio)tin(II) and *ate*-Complexes [(Me₃Si)₃CE(μ-SBu)₂Li(THF)₂] (E = Ge, Sn). Synthesis and Structure

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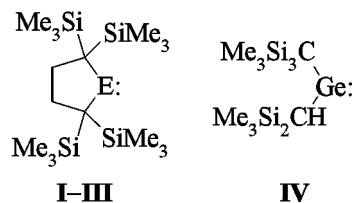
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Abstract—By reaction of Me₃SiSBu with anhydrous tin(II) chloride bis(butylthio)tin was obtained that exemplified a coordination polymer [Sn(SBu)₂]_n, whose elementary unit contained according to X-ray diffraction study three independent four-membered rings Sn₂S₂ of unusual geometry. It was demonstrated that polymeric thiolates [E(SBu)₂]_n (E = Ge, Sn) readily reacted with TsiLi (Tsi = C(SiMe₃)₃) in a mixed solvent ether THF affording in a good yield *ate*-complexes [(Me₃Si)₃CE(μ-SBu)₂Li(THF)₂]. Both complexes contain a four-membered ring in a *butterfly* conformation where the lithium atom is symmetrically bonded to both sulfur atoms, and the coordination polyhedra of Ge and Sn atoms may be regarded as distorted tetrahedra AB₃X, where one of coordination places is occupied by unshared electron pair. The structure of the *ate*-complexes observed in a crystal is conserved also in solution of nonpolar solvents.

Within the last decade the development of chemistry of the 4th group bivalent elements (Si, Ge, Sn, Pb) has been marked with a series of outstanding achievements [1–8]. Being heavy analogs of carbenes, dimethylsilylene [9–12], dimethylgermylene [13, 14], and dimethylstannylene [15] are stable only in cryogenic matrices at low temperatures, and like simple carbenes, they are characterized by extremely high reactivity. The attempts to synthesize bivalent compounds R₂E (E = Si, Ge, Sn) with the simplest substituents R (R = Me, Et, Ph etc.) have been carried out over a long period. For instance, the first publication on tin(II) chloride alkylation with organomagnesium compounds appeared in 1852 [16]. However it is now reliably established that depending on the synthesis procedure this reaction gives rise either to cyclooligomers (R₂E)_n or compounds with a trached chain containing R₂E, RE, and R₃E (E = Ge, Sn) fragments.

The modern stage of investigations on heavy carbene analogs stable under ordinary conditions started with the works of M. Lappert *et al.* [17]. This team synthesized and characterized by different physicochemical methods the first representatives of this class compounds, amino derivatives of germanium and tin E[N(SiMe₃)₂]₂. The first stable in the crystalline state dialkyl compounds: dialkylsilylene (**I**) [18], dialkylgermylenes (**II**) [19], (**IV**) [20], and dialkylstannylene (**III**) [21] were obtained relatively recently by using kinetic stabilization through introduction of bulky substituents linked to the elements under study.



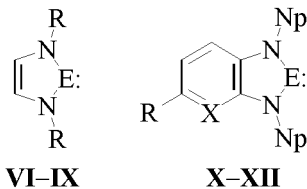
E = Si (**I**), Ge (**II**), Sn (**III**).

* For communication I see [28].

Also a number of stable diaryl derivatives Ar_2E ($\text{E} = \text{Ge}, \text{Sn}$) was prepared with spatially bulky aryls, for instance, 2,4,6-*t*-Bu₃C₆H₂ [22, 23], 2,6-Mes₂C₆H₃ [24], 2,4,6-(CF₃)₃C₆H₂ [25–27]. In preparation of heavy carbene analogs stable under ordinary conditions and of related compounds of germanium(II) and tin(II) alongside the sterical factors or instead of them are used also electronic factors. The main among the latter are listed below.

The introduction of σ -acceptor substituents with unshared electron pairs (Hlg, O, N, S) attached directly to the element provides stabilization on the one hand by reducing the MO energy occupied by the unshared electron pair on the element atom; on the other hand, the partial donation of the unshared electron pairs of the substituent to the vacant orbital of the element also contributes to the stabilization. However solely these factors only do not ensure formation of stable monomeric halo, alkoxy, amino, and alkylthio derivatives of bivalent silicon, germanium, and tin. The compounds obtained are as a rule coordination polymers or oligomers with $\text{E} \leftarrow \text{X}$ bonds.

On introducing into remote positions in the molecule of donor groups capable of forming intramolecular coordination bonds with the element atom its vacant orbital is involved in bonding, and therefore the electrophilicity of R_2E strongly decreases. We demonstrated in [28] that two coordination $\text{E} \leftarrow \text{N}$ bond allowed for existence of sufficiently stable monomeric germylenes and stannylenes $\text{E}(\text{OCH}_2\text{CH}_2\text{NMe}_2)_2$ ($\text{E} = \text{Ge}, \text{Sn}$) without spatially bulky groups attached to E atoms. The method of involving the vacant orbital located on the element atom into formation of a closed 6π -electron system of aromatic character was first used by Arduengo *et al.* [30] in the synthesis of carbene **VI** and thereafter it was successfully extended by many authors [3, 31–35] to the synthesis of its heavy analogs, e.g., compounds **VII–XII**.



$\text{E} = \text{C}, \text{R} = \text{Bu-}t$ (**VI**); $\text{E} = \text{Si}, \text{R} = \text{Bu-}t$ (**VII**); $\text{E} = \text{Ge}, \text{R} = \text{Bu-}t$ (**VIII**); $\text{E} = \text{Sn}, \text{R} = \text{Mes}$ (**IX**); $\text{E} = \text{Si}$ (**X**), Ge (**XI**), Sn (**XII**); $\text{X} = \text{C}, \text{N}$; $\text{R} = \text{H}, \text{Me}$.

In extension of our investigation of bivalent coordination compounds on germanium and tin [28, 29, 36] we report here the complete data on synthesis and structure of bis(butylthio)tin (**XIII**), and also of *ate*-complexes $[(\text{Me}_3\text{Si})_3\text{CE}(\mu\text{-SBu})_2\text{Li}(\text{THF})_2]$ [$\text{E} = \text{Ge}$ (**XIV**); $\text{E} = \text{Sn}$ (**XV**)] (preliminary communication see [29]). Bis(butylthio)tin (**XIII**) we obtained by reaction of Me_3SiSBu with tin(II) chloride analogously to procedure of bis(butylthio)germanium preparation described in [37]. Compound **XIII** is yellow crystalline substance, mp 49–51°C, well soluble in hydrocarbons and aromatic solvents.

According to our X-ray diffraction data compound **XIII** is a coordination polymer (Fig. 1) with $\text{Sn} \leftarrow \text{S}$ bonds. The structure contains three types of independent four-membered Sn_2S_2 constituting its elementary unit. The conformations of these rings are unusual. It is known [38], that four-membered rings E_2S_2 (E_2O_2) in dimeric $[\text{E}(\text{SR})_2]_2$ [39, 40] ($[\text{E}(\text{OR})_2]_2$ [40–47]), trimeric $[\text{E}(\text{SR})_2]_3$ [48], or polymeric $[\text{E}(\text{SR})_2]_n$ [40] ($[\text{E}(\text{OR})_2]_n$ [49]) compounds of bivalent 4th group elements ($\text{E} = \text{Ge}, \text{Sn}$ or Pb), as a rule exist only in two types of conformations: either in planar conformation with *anti*-periplanar location of substituents at the metal atoms [the substituents at sulfur (oxygen) atoms are placed in the ring plane] (Fig. 2a), or in a *butterfly* conformation with *syn*-periplanar position of substituents attached both to metal and sulfur (oxygen) atoms (Fig. 2b). Up till

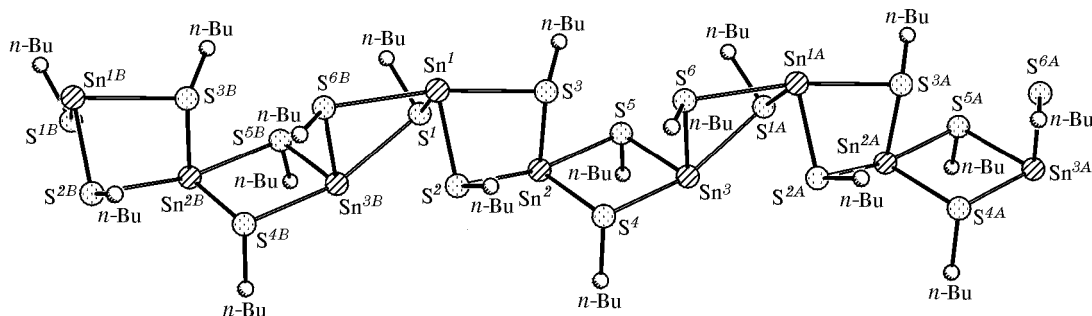


Fig. 1. Structure of polymer **XIII**; according to X-ray diffraction study.

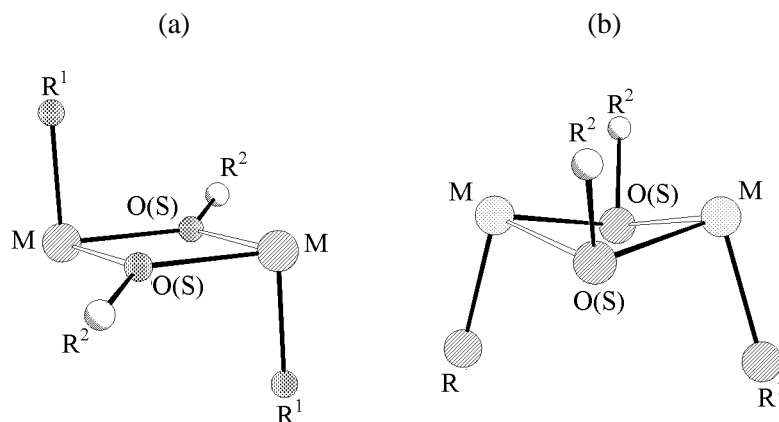


Fig. 2. Typical conformations of four-membered rings E_2S_2 (E_2O_2) in dimeric $[E(SR)_2]_2$ ($[E(OR)_2]_2$), trimeric $[E(SR)_2]_3$, and polymeric $[E(SR)_2]_n$ ($[E(OR)_2]_n$) compounds of bivalent 4th group ($E = \text{Ge, Sn or Pb}$); tubular lines indicate the coordination bonds: (a) planar conformation; (b) butterfly conformation.

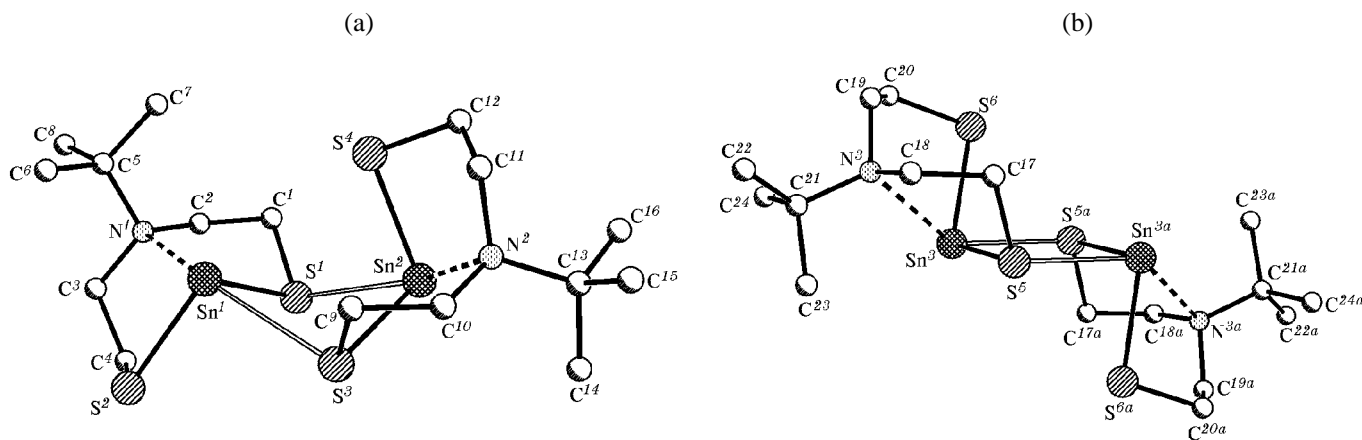


Fig. 3. Conformation of four-membered rings Sn_2S_2 in two crystallographically independent dimers $[\text{SnSCH}_2\text{CH}_2\text{NButCH}_2\text{CH}_2\text{S}]_2$ (a, b); tubular and dashed lines designate the coordination bonds.

now only two exceptions were known. In the dimer $[\text{SnSCH}_2\text{CH}_2\text{NButCH}_2\text{CH}_2\text{S}]_2$ [50] the four-membered ring Sn_2S_2 in one of two crystallographically independent molecules had planar conformation with *anti*-periplanar location of substituents attached both to tin and sulfur atoms (Fig. 3a); in the other molecule the ring was in *butterfly* conformation with *syn*-periplanar location of substituents at sulfur and *anti*-periplanar location of tin substituents (Fig. 3b). In a polymer $[\text{Pb}(\text{STol-}p)_2]_n$ (Tol-*p* = *p*-tolyl) [49] the four-membered ring Pb_2S_2 that constitutes the elementary unit has a butterfly conformation with an *anti*-periplanar location of substituents both at lead and sulfur atoms (Fig. 4). In its turn in polymer **XIII** we studied two of the three four-membered rings Sn_2S_2 in the elementary unit are in the *butterfly* conformation with the *anti*-periplanar location of substituents both at tin and sulfur atoms similar to the conformation of the four-membered ring Pb_2S_2 in

$[\text{Pb}(\text{STol-}p)_2]_n$ polymer (Fig. 5a, c), whereas the third ring takes the previously unknown planar conformation with a *syn*-periplanar position of substituents both at tin and sulfur atoms (Fig. 5b). Therefore it is

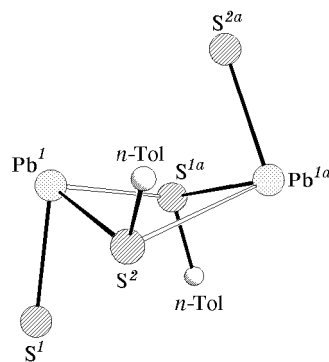


Fig. 4. Conformation of the four-membered ring Pb_2S_2 in $[\text{Pb}(\text{STol-}p)_2]_n$ polymer; tubular lines indicate the coordination bonds.

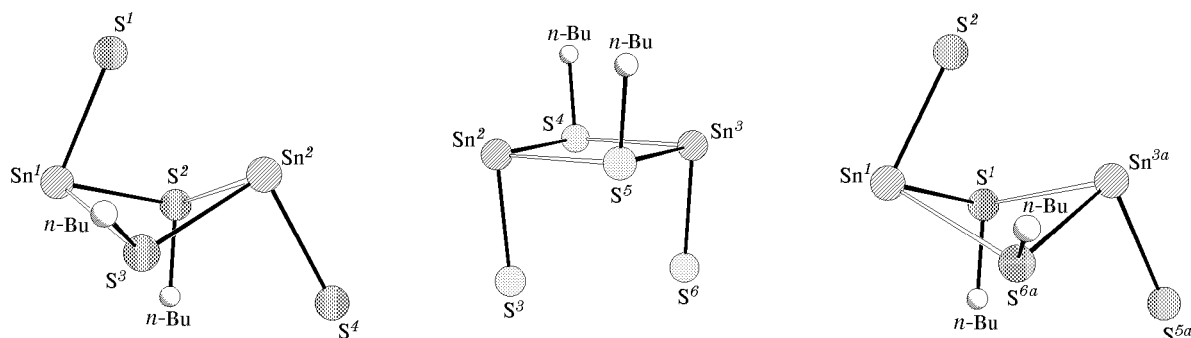
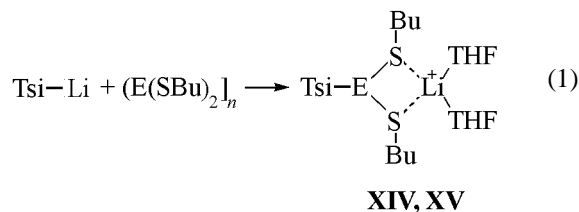


Fig. 5. Conformation of three independent four-membered rings Sn_2S_2 in polymer **XIII**; tubular lines indicate the coordination bonds.

tion with a *syn*-periplanar position of substituents both at tin and sulfur atoms (Fig. 5b). Therefore it is possible to conclude that the conformation of four-membered rings E_2S_2 (E_2O_2) in polymer compounds $[\text{E}(\text{SR})_2]_n$ ($[\text{E}(\text{OR})_2]_n$) of bivalent germanium, tin, and lead is more labile than in dimers $[\text{E}(\text{SR})_2]_2$ ($[\text{E}(\text{OR})_2]_2$) or trimers $[\text{E}(\text{SR})_2]_3$ ($[\text{E}(\text{OR})_2]_3$).

Both polymeric thiolates $[\text{E}(\text{SBu})_2]_n$ ($\text{E} = \text{Ge}, \text{Sn}$) readily react with TsiLi [$\text{Tsi} = \text{C}(\text{SiMe}_3)_3$] in a mixture of ether with THF affording in good yields ate-complexes **XIV** and **XV** (reaction 1). The complexes are light yellow crystalline compounds very sensitive to traces of air oxygen and moisture.



$\text{Tsi} = (\text{Me}_3\text{Si})_3\text{C}$; $\text{M} = \text{Ge}$ (**XIV**), Sn (**XV**).

Interestingly in this reaction the SBu group attached to the element is not replaced by trimethylsilyl moiety. This reaction occurs very readily with alkylthiolates of tin(IV). For instance, we established that TsiLi reacted with Et_3SnSBu under similar conditions with a rate of titration affording in almost quantitative yield Et_3SnTsi (**XVI**). However TsiLi did not react with Et_3GeSBu even at prolonged stirring of the reaction mixture although the organolithium and organomagnesium compounds, e.g., butyllithium [51] and ethylmagnesium bromide [52], easily cleave the Ge-S bond in R_3GeSR yielding the corresponding tetraalkyl derivatives of germanium. The structure of *ate*-complexes obtained **XIV** (Fig. 6) and **XV** (Fig. 7) and also of Et_3SnTsi (**XVI**) (Fig. 8) was established by X-ray diffraction study.

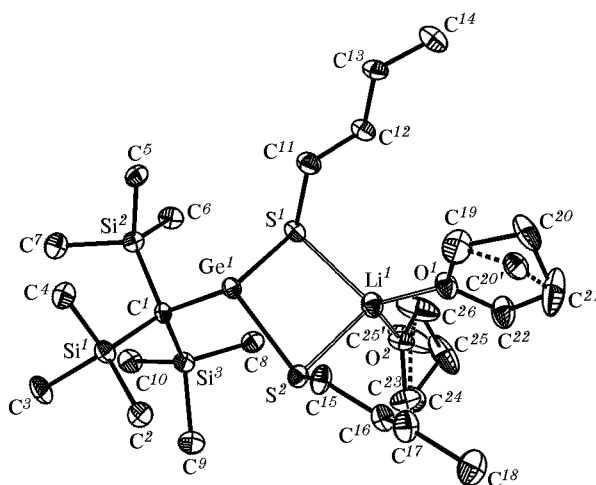


Fig. 6. The structure of *ate*-complex **XIV** with 50% probability ellipsoids of anisotropic displacements; dashed lines show the alternative positions of disordered oxygen atoms.

The structure of complexes **XIV** and **XV** underlie four-membered rings where the lithium atom is symmetrically bonded to two sulfur atoms. The rings are in the *butterfly* conformation. The bending angle along the diagonal line $\text{S}\cdots\text{S}$ is 22.3 in **XIV** and 45.8 in **XV**. Lithium atoms are situated in distorted tetrahedral surrounding between two sulfur atoms and two oxygens of coordinated THF molecules where the five-membered rings are in the envelop conformation. Coordination polyhedra of Ge and Sn atoms may be regarded as distorted tetrahedra AB_3X where in keeping with Gillespie rules one coordination place is occupied by an unshared electron pair. The tetrahedral configuration of the central carbon atom in the trimethylsilyl fragments is also distorted. The bond angles $\text{Si}^1\text{C}^1\text{E}$ and $\text{Si}^2\text{C}^1\text{E}$ are equal to 100.4 (3) and 105.7 (2) in **XIV** and 102.2(1) and 104.2 (1) in **XV** respectively due to the *trans*-effect [53]. The Sn-S

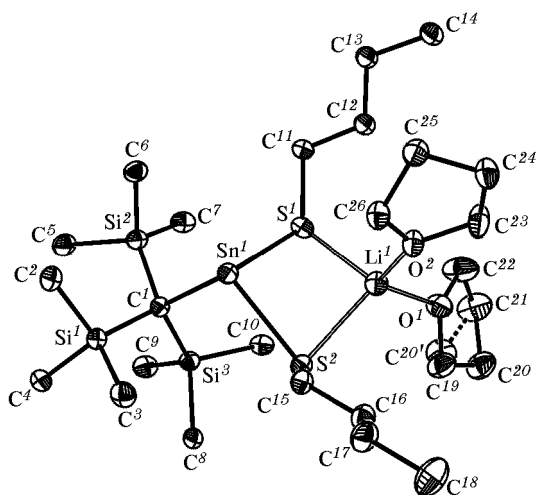


Fig. 7. Structure of ate-complex **XV** with 50% probability ellipsoids of anisotropic displacements; dashed lines show the alternative positions of disordered oxygen atoms.

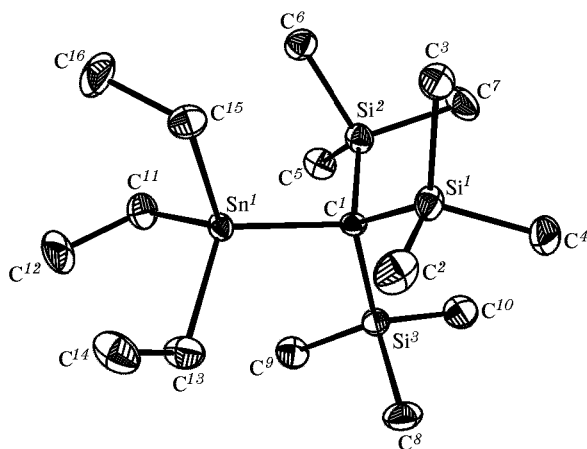


Fig. 8. Molecular structure of compound **XVI** with 50% probability ellipsoids of anisotropic displacements.

bonds in the tin ate-complex **XV** (Table 1) are longer than the Sn-S bonds in salt anion $[\text{Ph}_4\text{As}] + [\text{Sn}(\text{SPh})_3]^-$ [2.532 (1), 2.552 (1), 2.532 (1) Å] [54] but are of comparable length with the bridging bonds Sn-S in both four-membered rings of trimer $[\text{Sn}(\text{SAr})_2]_3$ (2.583, 2.588, 2.643, and 2.838 Å) [Ar = 2,6-di-(isopropyl)phenyl] [48]. The length of bonds E-C(Tsi) [2.096 (5) Å in **XIV** and 2.295 (3) Å in **XV**] is close to that observed in the other germylenes [55] and stannylenes [56] with trisilylmethyl groups. They are however considerably longer than typical interatomic distances observed in $\text{M}(\text{II})\text{-C}(\text{sp}^3)$ and $\text{M}(\text{IV})\text{-C}(\text{sp}^3)$ [38]. The Li-S distances [2.447(11) and 2.456 (11) Å in **XIV**, 2.483 (6) and 2.484 (6) Å in (**XV**)] are consistent with the expected length of $\text{Li}^+ \leftarrow \text{S}$ bond type [38]. The distances $\text{E} \cdots \text{Li}$ in ate-complexes **XIV**

Table 1. Principal bond lengths (d , Å) and bond angles (ω , deg) in compounds **XIV** and **XV**

Bond	Compound XIV , d	Compound XV , d
E-C	2.096 (5)	2.295 (3)
E-S1	2.393 (2)	2.568 (1)
E-S2	2.386 (2)	2.574 (1)
Li-S1	2.447 (9)	2.484 (6)
Li-S2	2.456 (9)	2.483 (6)
Li-O1	1.914 (11)	1.925 (7)
Li-O2	1.930 (10)	1.918 (6)
Angle	ω	ω
CE ¹	101.8 (2)	100.2 (1)
CE ²	103.3 (2)	102.6 (1)
SI ¹ ES ²	93.84 (5)	87.79 (3)
ES ¹ Li	85.7 (2)	81.6 (1)
ES ² Li	85.6 (2)	81.4 (2)
S ¹ LiO ²	114.8 (5)	115.6 (3)
S ² LiO ¹	118.6 (5)	114.4 (3)
ES ¹ C ¹¹	99.1 (2)	109.1 (1)
ES ² C ¹⁵	96.6 (2)	99.0 (1)
LiS ¹ C ¹¹	108.2 (3)	109.0 (2)
LiS ² C ¹⁵	101.3 (3)	106.0 (2)
O ¹ LiO ²	102.7 (5)	108.4 (3)
SLiS	90.8 (3)	91.7 (2)

[3.290 (9) Å] and **XV** [3.300 (6) Å] are determined by the geometric parameters of the four-membered rings, and they are significantly longer than in the known bonds Ge-Li or Sn-Li [38]. Note for comparison that the distance $\text{Sn} \cdots \text{Li}$ in $\text{LiSn}(\text{OR})_3$ [57] is 2.784 (4) Å.

The cyclic structure of compound **XIV** observed in crystals is conserved in solutions. In its ^1H NMR spectra in benzene- d_6 solution (360 MHz, 24°C) the SCH_2 groups appear as sharp peaks (AB-part of ABX_2 -sub-spectrum) with $^2J_{\text{AB}} = 12$; $^3J_{\text{AX}} = 3J_{\text{BX}} = 7.4$, $\text{AB} = 54.4$ Hz.

The structure in solutions of tin complex **XV** is more intricate. Under the same conditions the signals of SCH_2 groups appear as a strongly broadened singlet ($\Delta\nu = \sim 50$ Hz). In toluene- d_8 at 24°C (300 MHz) a multiplet is observed with $^2J_{\text{AB}} = 12$; $^3J_{\text{AX}} = ^3J_{\text{BX}} = 7.5$; $\text{AB} = 21.5$ Hz, and at -40°C appear sharp peaks (AB-part of ABX_2 -sub-spectrum) with $^2J_{\text{AB}} = 12$; $^3J_{\text{AX}} = ^3J_{\text{BX}} = 7.5$; $\text{AB} = 32.3$ Hz). Raising the temperature in the range from -40 to +50°C caused in the ^1H NMR spectrum of compound **XV** gradual decrease in the chemical shift difference corresponding to diastereotopic protons

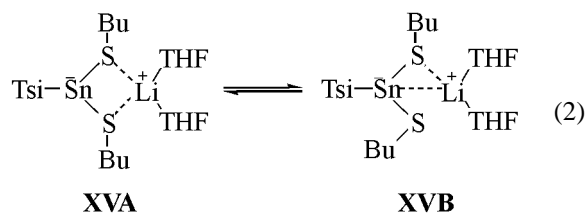
Table 2. Chemical shifts of diastereotopic protons of S-CH₂ groups in the ¹H NMR spectra, chemical shifts and lines width of ¹¹⁹Sn in the ¹¹⁹Sn NMR spectrum of *ate*-complex **XV** at different temperatures

<i>t</i> , °C	AB Hz (300 MHz)	Chemical shift ¹¹⁹ Sn, ppm	Line width, (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

(see Table. 2). The observed spectral changes are reversible.

Since within all temperature range studied the resonance lines remain narrow the observed changes in ν_{AB} indicate that in solution of compound **XV** an equilibrium nondegenerate dynamic process takes place whose rate is fast in the NMR time scale. In the course of the process the protons of the CH₂ group exchange their positions or the difference between their chemical shifts is reduced. It is also clear that in the equilibrium isomeric structures of similar stability take part (the ΔG° is small).

Presumably this pattern of temperature dependence may be caused by reversible dissociation of compound **XV** into (BuS)₂Sn and TsiLi. However this equilibrium was apparently lacking in the deuterio-toluene solution, at least as a fast process, since the signals of a small impurity of (BuS)₂Sn that was present in the sample (about 2–3%) were not broadened and did not change the position, form, and intensity at temperature variation. We believe that the most logical explanation is an assumption of an equilibrium (2) between two cyclic forms **XVA** and **XVB** which should be regarded as tight ion pairs of different structure. In the process one of the coordination S←Li bonds is ruptured, therewith the rotation around the S←C bond in this group gets free, and the diastereotopic protons therein exchange their positions. The energy loss at the cleavage of the S–C bond in this group is apparently partially compensated by approach of Li⁺ ion to the tin atom possessing an unshared electron pair.



To prove this assumption we measured the ¹H NMR spectra of complex **XV** in solution THF-*d*₈. In this strongly coordinating solvent the ABX₂-sub-spectrum collapsed into an A₂X₂ spectrum, and the proton signals from SCH₂ groups appeared at room temperature as sharp triplets (³J_{HH} = 7.3 Hz) evidencing marked acceleration of the exchange process (2).

In the ¹¹⁹Sn NMR spectrum of complex **XV** exists a single signal at 275.24 ppm. On cooling the signal somewhat shifted upfield, and its line width notably decreased (Table 2). This behavior also testifies to the ion-pair equilibrium (2).

The data presented above are a strong argument for structural identity of complexes **XIV** and **XV** in crystal and solution.

Thus we prepared by reaction of Me₃SiSBU with anhydrous tin(II) chloride bis(butylthio)tin as a coordination polymer [Sn(SBU)₂]_n, which according to X-ray diffraction study contained three types of independent four-membered Sn₂S₂ rings of unusual geometry. Polymeric thiolates [E(SBU)₂]_n (E = Ge, Sn) readily take up TsiLi [Tsi = C(SiMe₃)₃] in an ether THF mixture affording in good yield *ate*-complexes [(Me₃Si)₃CE(μ-SBU)₂Li(THF)₂]. Both complexes contain the four-membered ring in *butterfly* conformation where the lithium atom is symmetrically bonded to both sulfur atoms, and the coordination polyhedra of Ge and Sn atoms may be regarded as distorted tetrahedra AB₃X where one coordination place is occupied by an unshared electron pair.

EXPERIMENTAL

¹H, ¹³C, ⁷Li, ²⁹Si and ¹¹⁹Sn NMR spectra were registered on spectrometers Bruker DPX-300 and Bruker AM-360. Chemical shifts in the ¹H and ¹³C NMR spectra were measured in ppm from solvent signals with the accuracy of ±0.01, ±0.05 ppm respectively and were recalculated into the standard δ -scale by common expressions. ²⁹Si, ¹¹⁹Sn, and ⁷Li NMR spectra were registered with respect to TMC (²⁹Si), Me₄Sn (¹¹⁹Sn), and LiCl in D₂O as

external references with the accuracy of ± 0.1 , ± 0.2 , and $\times 2$ ppm respectively. The coupling constants are presented with accuracy of ± 0.1 Hz. The assignment of signals in ^{13}C NMR spectra was performed with the use of APT procedure.

All procedures were carried out in a vacuum of 10^{-3} mm Hg using the standard Schlenk technique under atmosphere of dry argon or in fully sealed vessels with breakable glass membranes and in ampules. The commercial C_6D_6 , toluene- d_8 and THF- d_8 (Russia) were boiled over LiAlH_4 under an argon atmosphere, the solvents were condensed through a vacuum manifold directly into the reactor. The initial compounds TsiH [58], TsiLi [59, 60], Me_3SiSBu [61], Et_3GeSBu [62], Et_3SnSBu [63], dioxanate of Ge(II) chloride [64], and $\text{Ge}(\text{SBu})_2$ [37] used in the study were prepared by published procedures. The constants of compounds obtained were identical to the published data.

Synthesis of bis(butylthio)tin $[\text{Sn}(\text{SBu})_2]_n$ (XIII).

A mixture of freshly prepared anhydrous SnCl_2 (2.63 g, 13.9 mmol) and Me_3SiSBu (6.62 g, 40.9 mmol) in 25 ml of THF was heated at reflux for 1 h. The volatile products and solvent were removed at $20^\circ\text{C}/1$ mm Hg and then at $100^\circ\text{C}/1$ mm Hg. The residue was crystallized from hexane. We obtained 3.66 g (90%) of needle crystals of yellow color, mp $49\text{--}51^\circ\text{C}$ (in a sealed capillary). ^1H NMR spectrum (C_6D_6), δ , ppm (J , Hz): 0.95 t (6H, CH_3 , $^3J_{\text{HH}}$ 7.3), 1.45–1.55 m (4H, CH_2), 1.82 m (4H, CH_2), 3.16 br.m (4H, SCH_2). ^{119}Sn NMR spectrum (C_6D_6), δ , ppm: 38.34. Found, %: C 32.08; H 6.01. $\text{C}_8\text{H}_{18}\text{S}_2\text{Sn}$. Calculated, %: C 32.35; H 6.11.

Preparation of $[(\text{Me}_3\text{Si})_3\text{CGe}(\mu\text{-SBu})_2\text{Li}(\text{THF})_2]$ (XIV). A solution of LiTsi (3.68 g, prepared from 15.9 mmol TsiH in 33 ml of THF and 5.7 ml of 2.8 N MeLi solution in Et_2O) was added at room temperature while stirring to a solution of $\text{Ge}(\text{SBu})_2$ (3.98 g, 15.9 mmol) in 20 ml of THF. The mixture was stirred at room temperature for 1 h, and then the solvent was removed in a vacuum. The oily dark-red residue was extracted with 50 ml of pentane, the extract was evaporated to 30 ml volume and left standing at -12°C . We obtained 4.0 g (40%) of compound XIV as light-yellow crystals, mp $80\text{--}81^\circ\text{C}$ (decomp.). The analytical data show that one THF molecule is easily lost when the sample is dried for analysis. ^1H NMR spectrum (C_6D_6), δ , ppm (J , Hz): 0.71 s (27H, $^2J_{\text{SiH}}$ 6.0), 1.00 t (6H, $^3J_{\text{HH}}$ 7.3), 1.41–1.59 m (12H, CH_2 and THF), 1.64–1.85 m (4H, CH_2), 2.73–2.96 m (4H, SCH_2 , AB-part of spin system ABX_2 , $^2J_{\text{AB}}$ 12; $^3J_{\text{AX}} = ^3J_{\text{BX}}$ 7.4; $\Delta\nu_{\text{AB}}$

54.4 Hz), 3.62 m (8H, OCH_2 , THF). ^{13}C (C_6D_6) δ , ppm (J , Hz): 5.9 s (Me_3Si , $^1J_{\text{SiC}}$ 50.2), 14.2 s (CH_3), 14.3 s (CSi_3 , $^1J_{\text{SiC}}$ 35.4), 22.9 s (CH_2), 25.3 s (CH_2 , THF), 33.0 s (CH_2), 36.7 s (SCH_2), 68.4 s (OCH_2 , THF). ^7Li (C_6D_6), δ , ppm: 0.78. ^{29}Si NMR spectrum (C_6D_6), δ , ppm: 3.2. Found, %: C 47.1; H 9.9. $\text{C}_{22}\text{H}_{53}\text{LiOS}_2\text{Si}_3\text{Ge}$. Calculated, %: C 47.0; H 9.5.

Preparation of $[(\text{Me}_3\text{Si})_3\text{CSn}(\mu\text{-SBu})_2\text{Li}(\text{THF})_2]$ (XV). The compound was synthesized as described above for $[(\text{Me}_3\text{Si})_3\text{CGe}(\mu\text{-SBu})_2\text{Li}(\text{THF})_2]$ (XIV) from 3.45 g (11.6 mmol) of $\text{Sn}(\text{SBu})_2$ in 22 ml of THF and solution of TsiLi (3.24 g, prepared from 14.0 mmol of TsiH in 17 ml of THF and 5 ml of 2.8 N solution of MeLi in Et_2O). On removing the solvents the oily light-yellow residue was extracted with 20 ml of pentane, evaporated in a vacuum to a half of the initial volume, filtered, and the filtrate was cooled to 12°C . We obtained 4.77 g (60%) of compound XV as light-yellow crystals, mp $45\text{--}47^\circ\text{C}$ (from 34°C the compound starts to darken). We failed to get plausible elemental analysis data because of exceedingly high sensitivity of the compound to the traces of air oxygen and moisture. ^1H NMR spectrum (C_6D_6), δ , ppm (J , Hz): 0.69 s (27H, SiMe_3 , $^2J_{\text{SiH}}$ 6.1), 0.99 t (6H, CH_3 , $^3J_{\text{HH}}$ 7.4), 1.32–1.63 br.m (12H, CH_2 + THF), 1.81 br.m (4H, CH_2), 2.89 br.s (4H, SCH_2), 3.66 br.m (8H, OCH_2 , THF). ^1H NMR spectrum ($\text{C}_6\text{D}_5\text{CD}_3$), δ , ppm (J , Hz): 0.44 s (27H, SiMe_3), 0.87 t (6H, CH_3 , $^3J_{\text{HH}}$ 7.4), 1.31–1.44 m (4H, CH_2), 1.49 m (8H, CH_2 and THF), 1.53–1.67 m (4H, CH_2), 2.55–2.72 br.m (4H, SCH_2 , AB-part of spin system ABX_2 , $^2J_{\text{AB}}$ 12; $^3J_{\text{AX}} = ^3J_{\text{BX}}$ 7.5; $\Delta\nu_{\text{AB}}$ 21.5 Hz), 3.56 m (8H, OCH_2 , THF). ^1H NMR spectrum (THF- d_8), δ , ppm (J , Hz): 0.35 s (27H, SiMe_3), 1.02 t (6H, CH_3 , $^3J_{\text{HH}}$ 7.3), 1.51–1.64 m (4H, CH_2), 1.66–1.82 m (4H, CH_2), 2.71 br.t (4H, SCH_2 , $^3J_{\text{HH}}$ 7.3). ^{13}C NMR spectrum, ppm (J , Hz): 6.28 s (Me_3Si , $^1J_{\text{CSi}}$ 50.0), 14.11 (CH_3), 17.70 (CSi_3), 22.6 (CH_2), 25.4 (THF), 31.1 br. (CH_2), 37.6 br. (CH_2S), 68.5 (OCH_2 , THF). ^{29}Si NMR spectrum ($\text{C}_6\text{D}_5\text{CD}_3$), δ , ppm (J , Hz): 3.15 ($^1J_{\text{SiC}}$ 50.0; $^2J_{\text{SiSn}}$ 43.5). ^{119}Sn NMR spectrum ($\text{C}_6\text{D}_5\text{CD}_3$), δ , ppm: 275.3. ^7Li (C_6D_6), δ , ppm: 0.93.

Reaction of TsiLi with Et_3SnSBu . A solution of TsiLi, obtained from TsiH (0.3399 g, 1.47 mmol) in THF (1.5 ml) and 0.54 ml of 2.69 N solution of MeLi in Et_2O was added while stirring at $\sim 20^\circ\text{C}$ to a solution of Et_3SnSBu (0.4318 g, 1.47 mmol) in 2 ml of THF. The mixture was stirred for 15 min, the solvent was removed in a vacuum. The residue was extracted with CDCl_3 . According to NMR data the solution contained Et_3SnTsi (XVI) (94%) and TsiH (6%). For XVI: ^1H NMR spectrum (CDCl_3), δ , ppm

Table 3. Main crystallographic data and refining parameters for compounds **XIII–XVI**

Parameters / Compound no.	XIII	XIV	XV	XVI
Empirical formula	C ₂₄ H ₅₄ S ₆ Sn ₃	C ₂₆ H ₆₁ LiO ₂ Si ₃ S ₂ Ge	C ₂₆ H ₆₁ LiO ₂ Si ₃ S ₂ Sn	C ₁₆ H ₄₂ Si ₃ Sn
Molecular weight	891.10	633.67	679.77	437.46
<i>T</i> , K	153	100	100	120
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	P21/n	P21/c	P21/n	P21/c
<i>a</i> , Å	17.222 (3)	14.345 (2)	12.2299 (7)	13.991 (10)
<i>b</i> , Å	9.264 (2)	18.105 (2)	16.9483 (9)	10.362 (7)
<i>c</i> , Å	23.030 (5)	13.963 (2)	18.2285 (10)	15.873 (13)
β, deg	96.87 (3)	90.452 (3)	104.979 (1)	91.03 (2)
<i>V</i> , Å ³	3647.7 (13)	3626.2 (7)	3649.9 (3)	2301 (3)
<i>Z</i>	4	4	4	4
<i>d</i> _c , g cm ⁻³	1.623	1.161	1.237	1.263
<i>F</i> (000)	1776	1368	1440	920
μ, mm ⁻¹	2.394	1.079	0.932	1.260
2θ _{max} , deg	46	60	58	50
Number of measured reflections	5237	28753	26129	17905
Number of independent reflections	5042	10430	8759	4047
Number of reflections with <i>I</i> > 2σ(<i>I</i>)	2651	4459	6349	3213
Number of refined parameters	353	334	336	193
<i>R</i> ₁ (<i>I</i> > 2σ(<i>I</i>))	0.1245	0.0804	0.0517	0.0857
w <i>R</i> ₂ (all data)	0.2714	0.1794	0.1311	0.2296
GOF	1.078	0.951	1.001	1.019
<i>T</i> _{min} ; <i>T</i> _{max}	–	0.694; 1.00	0.738; 1.00	0.683; 0.882

(*J*, Hz): 0.17 s (27H, Me₃Si, ²*J*_{H_{Si}} 6.1), 1.01–1.18 m (6H, CH₂Sn), 1.21–1.39 m (9H, CH₃CH₂Sn). ¹H NMR spectrum (C₆D₆), δ, ppm: 0.29 s (27H, Me₃Si), 0.9–1.73 m (15H, CH₃CH₂Sn). ¹³C NMR spectrum (CDCl₃), δ, ppm (*J*, Hz): –0.53 (CSi₃, ¹*J*_{CSn} 33/43), 5.36 (Me₃Si, ¹*J*_{CSi} 51, ³*J*_{CSn} 13), 6.73 (CH₂Sn, ¹*J*_{CSn} 309/324), 11.34 (CH₃CH₂Sn, ²*J*_{CSn} 22). ¹³C NMR spectrum (C₆D₆), δ, ppm (*J*, Hz): –0.27 (CSi₃, ¹*J*_{CSn} 33/43), 5.73 (Me₃Si, ¹*J*_{CSi} 51, ³*J*_{CSn} 13), 7.22 (CH₂Sn, ¹*J*_{CSn} 309/324), 11.70 (CH₃CH₂Sn, ²*J*_{CSn} 22). ²⁹Si NMR spectrum (C₆D₆), δ, ppm: 0.94. Found, %: C 50.11; H 9.65. C₁₆H₄₂Si₃Sn. Calculated, %: C 43.9; H 9.7. After recording of spectra and removing the solvent sublimation at 80–90°C/10⁻³ mm Hg afforded crystals suitable for X-ray diffraction analysis. For Et₃SnSBu: ¹H NMR spectrum (C₆D₆), δ, ppm (*J*, Hz): 0.9 t (3H, CH₃, ³*J*_{HH} 7.3), 0.94–1.13 m (6H, CH₂Sn), 1.14–1.37 m (9H, CH₃CH₂Sn), 1.38–1.50 m (2H, CH₂), 1.55–1.65 m (2H, CH₂), 2.57 t (2H, CH₂SSn, ³*J*_{HH} 7.2). ¹³C NMR spectrum (CDCl₃), δ, ppm (*J*, Hz): 4.55 (CH₂Sn, ¹*J*_{CSn} 322/338), 10.55 (CH₃CH₂Sn, ²*J*_{CSn} 25), 13.59 (CH₃), 21.78 (CH₂), 26.20 (CH₂), 37.10 (CH₂SSn). ¹³C (C₆D₆), δ, ppm (*J*, Hz): 4.87 (CH₂Sn, ¹*J*_{CSn} 323/338), 10.88 (CH₃CH₂Sn, ²*J*_{CSn}

25), 13.91 (CH₃), 22.15 (CH₂), 26.56 (CH₂, ³*J*_{CSn} 15), 37.64 (CH₂SSn, ²*J*_{CSn} 12.5).

Reaction of TsiLi with Et₃GeSBu. A solution of TsiLi, obtained from TsiH (0.59 g, 2.54 mmol) in THF (2.5 ml) and 0.95 ml of 2.69 N solution of MeLi in Et₂O was added while stirring at ~20°C to a solution of Et₃GeSBu (0.6418 g, 2.58 mmol) in 2 ml of THF. The mixture was stirred for 1 h and left overnight. Then 0.45 g of Me₃SiCl was added, the mixture was stirred for 15 min, the solvents were removed in a vacuum. The residue was extracted with C₆D₆. According to NMR data the solution contained Et₃GeSBu, (Me₃Si)₄C, and TsiH in a molar ratio 1:0.5:0.5. Melting point and ¹H and ¹³C NMR data for (Me₃Si)₄C are in agreement with those published [65]. For Et₃GeSBu: ¹H NMR spectrum (C₆D₆), δ, ppm (*J*, Hz): 0.91 t (3H, CH₃, ³*J*_{HH} 7.3), 0.99 m (6H, CH₂Ge), 1.12 m (9H, CH₃CH₂Ge), 1.39–1.52 m (2H, CH₂), 1.55–1.68 m (2H, CH₂), 2.48 t (2H, CH₂SGe, ³*J*_{HH} 7.2). ¹³C NMR spectrum (C₆D₆), δ, ppm: 7.57 (CH₂Ge), 8.99 (CH₃CH₂Ge), 13.93 (CH₃), 22.15 (CH₂), 26.17 (CH₂), 35.61 (CH₂SGe).

X-ray diffraction study. Parameters of unit cell and intensities of reflections were measured on

automatic diffractometers Syntex P2₁ (compound **XIII**) and Bruker SMART CCD 1000 (compounds **XIV–XVI** [λMoK_α -radiation, graphite monochromator, $\theta/2\theta$ (**XIII**) and ω (**XIV–XVI**) scanning]). For compounds **XIV–XVI** the absorption of X-rays was taken into account using SADABS routine [66]. The principal crystallographic data of compounds **XIII–XVI** are listed in Table 3. The structures of all compounds were solved by the direct method and refined by the full-matrix least-squares procedure in anisotropic approximation for nonhydrogen atoms. The fragments of butyl groups C⁷–C⁸, C¹⁰–C¹¹ and C²¹–C²² in compound **XIII** are disordered by two positions with respective population density 0.5:0.5, 0.5:0.5, and 0.7:0.3. The carbon atoms C²⁰ and C²⁵ belonging to the THF molecules in compound **XIV** and atom C²⁰ in compound **XV** are also disordered by two positions each with respective population densities 0.7:0.3, 0.6:0.4, and 0.7:0.3. The positions of hydrogen atoms in all compounds are geometrically calculated and refined in isotropic approximation with fixed position (rider model) and thermal [$U_{\text{iso}}(\text{H}) = 1.5 U_{\text{eq}}(\text{C})$ for CH₃ groups and $U_{\text{iso}}(\text{H}) = 1.2 U_{\text{eq}}(\text{C})$ for all other groups] parameters. All calculations were performed with the use of SHELXTL PLUS (Version 5.10) software [67]. The tables of atomic coordinates, bond lengths, bond angles, anisotropic thermal parameters for compounds **XIII–XVI** are deposited to Cambridge Crystallographic Databank.

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REFERENCES

- Bogdanov, S.E., Egorov, M.P., Faustov, V.I., and Nefedov, O.M., *The chemistry of organic germanium, tin and lead compounds*, Rappoport, Z., Ed., Chichester: Wiley, 2002.
- Gehrhus, B. and Lappert, M.F., *J. Organomet. Chem.*, 2001, vol. 617–618, p. 209.
- Haaf, N., Schmedake, T.A., and West, R., *Acc. Chem. Res.*, 2000, vol. 33, p. 704.
- Tokitoh, N. and Okazaki, R., *Coord. Chem. Rev.*, 2000, 210, p. 251.
- Weidenbruch, M., *Eur. J. Inorg. Chem.*, 1999, p. 373.
- Barrau, J. and Rima, G., *Coord. Chem. Rev.*, 1998, vols. 178–180, p. 593.
- Gaspar, P.P. and West, R.V., *The chemistry of Organic Silicon Compounds*, Rappoport, Z. and Apeloig, Y., Eds., John Wiley & Sons: Chichester, 1998, vol. 2, pt. 3, p. 2483.
- Lappert, M.F., *Main Group Metal. Chem.*, 1994, vol. 17, p. 183.
- Drahnak, N.J., Michl, J., and West, R., *J. Am. Chem. Soc.*, 1979, vol. 101, p. 5427.
- Baggott, J.E., Blitz, M.A., Frey, H.M., Lightfoot, P.D., and Walsh, R., *J. Chem. Soc., Faraday Trans.*, 1998, vol. 84, p. 515.
- Baggott, J.E., Blitz, M.A., Frey, H.M., and Walsh, R., *J. Am. Chem. Soc.*, 1990, vol. 112, p. 8337.
- Al-Rubaiey, N., Carpenter, I.W., Walsh, R., Becerra, R., and Gordon, M.S., *J. Phys. Chem. A*, 1998, vol. 102, p. 8564.
- Becerra, R., Bogdanov, S.E., Egorov, M.P., Lee, V.Ya., Nefedov, O.M., and Walsh, R., *Chem. Phys. Lett.*, 1996, vol. 250, p. 111.
- Becerra, R., Egorov, M.P., Krylova, I.V., Nefedov, O.M., and Walsh, R., *Chem. Phys. Lett.*, 2002, vol. 351, p. 47.
- Becerra, R., Bogdanov, S.E., Egorov, M.P., Faustov, V.I., Krylova, I.V., Nefedov, O.M., and Walsh, R., *J. Am. Chem. Soc.*, 2002, vol. 124, p. 7555.
- Lowig, C., *Ann.*, 1852, vol. 84, p. 308.
- Davidson, P.J., Harris, D.H., and Lappert, M.F., *J. Chem. Soc. Dalton*, 1976, p. 2268.
- Kira, M., Ishida, S., Iwamoto, T., and Kabuto, C., *J. Am. Chem. Soc.*, 1999, vol. 121, p. 9722.
- Kira, M., Ishida, S., Iwamoto, T., Ichinohe, M., Kabuto, C., Ignatovich, L., and Sakurai, H., *Chem. Lett.*, 1999, p. 263.
- Jutzi, P., Becker, A., Stammli, H.G., and Nemmann, B., *Organometallics*, 1991, vol. 10, p. 1647.
- Kira, M., Yauchibara, R., Hirano, R., Kabuto, C., and Sakurai, H., *J. Am. Chem. Soc.*, 1991, vol. 113, p. 7785.
- Jutzi, P., Schmidt, H., Nemmann, B., and Stammli, H.G., *Organometallics*, 1996, vol. 15, p. 741.
- Weidenbruch, M., Schlaefke, J., Schafer, A., Peters, K., Schnering, H.G.v., and Marsmann, H., *Angew. Chem. Int. Ed.*, 1994, vol. 33, p. 1846.
- Simons, R.S., Pu, L., Olmstead, M.M., and Power, P.P., *Organometallics*, 1997, vol. 16, p. 1920.
- Bender, IV, J., Holl, M.M.B., and Kamp, J.W., *Organometallics*, 1997, vol. 16, p. 2743.
- Grutzmacher, H., Pritzkow, H., and Edelmann, F.T., *Organometallics*, 1991, vol. 10, p. 23.
- Bigwood, M.P., Corvan, P.J., and Zuckerman, J.J., *J. Am. Chem. Soc.*, 1981, vol. 103, p. 7643.
- Zemlyanskii, N.N., Borisova, I.V., Kuznetsova, M.G., Khrustalev, V.N., Ustynyuk, Yu.A., Nechaev, M.S., Lunin, V.V., Barrau, J., and Rima, G., *Organometallics*, 2003 (in press).

29. Borisova, I.V., Eaborn, C., Hill, M.S., Khrustalev, V.N., Kuznetzova, M.G., Smith, J.D., Ustyynyuk, Yu.A., Lunin, V.V., and Zemlyansky, N.N., *Organometallics*, 2002, vol. 21, p. 4005.
30. Arduengo, III, A.J., Harlow, R.L., and Kline, M., *J. Am. Chem. Soc.*, 1991, vol. 113, p. 361.
31. Hermann, W.A., Denk, M., Behm, J., Scherer, W., Klingan, F.-R., Bock, H., Solouki, B., and Wagner, M., *Angew. Chem.*, 1992, vol. 104, p. 1489; *Angew. Chem. Int. Ed.*, 1992, vol. 31, p. 1485.
32. Gans-Eischler, N., Guetat, D., and Nieger, M., *Angew. Chem. Int. Ed. Engl.*, 2002, vol. 41, p. 1888.
33. Gehrhus, B. and Lappert, M.F., *J. Organomet. Chem.*, 2001, vols. 617–618, p. 209.
34. Heinicke, J., Oprea, A., Kindermann, M.K., Karpatis, T., Nyulaszi, L., and Veszpremi, T., *Chem. Eur. J.*, 1998, vol. 4, p. 541.
35. Al-Juaid, S.S., Avent, A.G., Eaborn, C., Hill, M.S., Hitchcock, P.B., Patel, D.J., and Smith, J.D., *Organometallics*, 2001, vol. 20, p. 1223.
36. Khrustalev, V.H., Borisova, I.V., Zemlyanskii, H.H., Ustyynyuk, Yu.A., and Antipin, M.Yu., *Kristallografiya*, 2002, vol. 47, p. 672.
37. Jutzi, P. and Steiner, W., *Chem. Ber.*, 1976, vol. 109, p. 1575.
38. *Cambridge Crystallographic Database*, Release 2002. Cambridge.
39. Hitchcock, P.B., Jasim, H.A., Kelly, R.E., and Lappert, M.F., *Chem. Commun.*, 1985, p. 1776.
40. Veith, M., Hobein, P., and Rosler, R., *Z. Naturforsch. Teil B*, 1989, vol. 44, p. 1067.
41. Fjeldberg, T., Hitchcock, P.B., Lappert, M.F., Smith, S.J., and Thorne, A., *J. Chem. Commun.*, 1985, p. 939.
42. Zybill, C. and Muller, G., *Z. Naturforsch. Teil B*, 1989, vol. 43, p. 45.
43. McGeary, M.J., Folting, K., and Caulton, K.G., *Inorg. Chem.*, 1989, vol. 28, p. 4051.
44. Teff, D.J., Huffman, J.C., and Caulton, K.G., *Inorg. Chem.*, 1995, vol. 34, p. 2491.
45. Veith, M., Mathur, C., and Huch, V., *J. Chem. Soc. Dalton Trans.*, 1997, p. 995.
46. Van, Zandt, W., Huffman, J.C., and Stewart, J.T., *Main Group Metal Chemistry*, 1998, vol. 21, p. 237.
47. McBurnett, B.G. and Cowley, A.H., *Chem. Commun.*, 1999, p. 17.
48. Hitchcock, P.B., Lappert, M.F., Samways, B.J., and Weinberg, E.L., *Chem. Commun.*, 1983, p. 1492.
49. Goel, S.C., Chiang, M.Y., and Buhro, W.E., *Inorg. Chem.*, 1990, vol. 29, p. 4640.
50. Jurkshat, K., Scheer, M., Tzschach, A., Meunier-Piret, J., and Van, Meerssche, M., *J. Organomet. Chem.*, 1985, vol. 28, p. 173.
51. Hooton, K.A. and Allred, A.L., *Inorg. Chem.*, 1965, vol. 4, p. 671.
52. Satge, J. and Lisbre, M., *Bull. Soc. Chim. France*, 1965, p. 2578.
53. Slovokhotov, Yu.L., Timofeeva, T.V., Antipin, M.Yu., and Struchkov, Yu.T., *Journal of Molecule Structure*, 1984, vol. 112, p. 127.
54. Dean, P.A.W., Vittal, J.J., and Payne, N.C., *Can. J. Chem.*, 1985, vol. 63, p. 394.
55. Jutzi, P., Becker, A., Leue, C., Stammeler, H.G., and Neumann, B., *Organometallics*, 1991, vol. 10, p. 3838.
56. Eaborn, C., Hitchcock, P.B., Smith, J.D., and Sozerli, S.E., *Organometallics*, 1997, vol. 16, p. 5653.
57. Smith, G.D., Fanwick, P.F., and Rothwell, I.P., *Inorg. Chem.*, 1989, p. 618.
58. Merker, R.L. and Scott, M.J., *J. Am. Chem. Soc.*, 1963, vol. 85, p. 2243.
59. Aiube, Z.H. and Eaborn, C., *J. Organomet. Chem.*, 1984, vol. 269, p. 217.
60. Draher, S.M., Eaborn, C., and Smith, J.D., *J. Organomet. Chem.*, 1988, vol. 355, p. 33.
61. Langer, S.H., Cpnell, S., and Wender, J., *J. Org. Chem.*, 1958, vol. 23, p. 50.
62. Satge, J. and Lesbre, M., *Bull. Soc. Chim. France*, 1962, p. 703.
63. Sasin, G.S., *J. Org. Chem.*, 1953, vol. 18, p. 1142.
64. Fjeldberg, F., Haaland, A., Schilling, B.E.R., and Lappert, M.F., *J. Chem. Soc. Dalton*, 1986, p. 1551.
65. Zemlyanskii, H.H. and Sokolikova, O.K., *Zh. Analit. Khim.*, 1981, vol. 36, p. 1990.
66. SMART and SAINT, Release 5.0. Area detector control and integration software, Bruker AXS, Analytical X-Ray Instruments, Madison, 1998.
67. Sheldrick, G.M., *SHELXTL, V5.10*, Madison: Bruker AXS Inc., 1997.