

Reaction of *N*-trimethylsilyl derivatives of amides and lactams with chloro(chloromethyl)dimethylstannane: Crystal and molecular structure of 1-(chlorodimethylstannylmethyl)-2-piperidone

Sergey Yu. Bylikin ^a, Aleksandr G. Shipov ^a, Vadim V. Negrebetsky ^a, Yuri I. Baukov ^{a,*}, Yuri E. Ovchinnikov ^b, Sergei A. Pogozhikh ^b, Sergei V. Pestunovich ^c, Lyudmila I. Belousova ^c, Elena F. Belogolova ^c, Valery F. Sidorkin ^c, Mikhail G. Voronkov ^c, Vadim A. Pestunovich ^{c,*}, Inna Kalikhman ^d, Daniel Kost ^d

^a Russian State Medical University, Ostrovityanov Street 1, Moscow 117869, Russia

^b Novosibirsk State Pedagogical University, Vilyuiskaya Street 28, Novosibirsk 630126, Russia

^c A.E. Favorsky Irkutsk Institute of Chemistry, Siberian Branch RAS, Favorsky Street 1, Irkutsk 664033, Russia

^d Department of Chemistry, Ben-Gurion University of the Negev, Beer Sheva 84105, Israel

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Abstract

A general scheme of reactions between chloro(chloromethyl)dimethylstannane and *N*-trimethylsilylamides and -lactams was established by NMR and IR techniques. The reactions proceed via transmetallation followed by transformation of the *N*-stannylated intermediate (**1**) into (*N*-Sn)-coordinated *O*-stannylmethyl (**2**) and (*O*-Sn)-coordinated *N*-stannylmethyl (**3**) derivatives. In the cases of 2-piperidone and 2-hexahydroazepinone these products were isolated as individual compounds (**2b,c** and **3b,c**). X-ray diffraction study of 1-(chlorodimethylstannylmethyl)-2-piperidone (**3b**) confirmed (3 + 2)-coordination state of the tin atom and axial positions of oxygen and halogen atoms. The experimental and quantum-chemically calculated structural parameters are discussed in comparison with those of related trigonal bipyramidal (TBP) silicon, germanium and tin derivatives. Calculation at the MP2/LanL2DZ/D95 level reveals that the stability of the (*O*-M)chelates increases in the following order: (*O*-Si) < (*O*-Ge) < (*O*-Sn).

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1. Introduction

The interest in penta- and hexacoordinated organotin derivatives, in particular compounds with intramolecular coordination, results from their high reactivity, structural and stereodynamic diversity. These properties have been used for modelling of the pathways of nucleophilic substitution at the tin atom [1]. However, at present only few

examples of pentacoordinated tin derivatives with intramolecular *O*-Sn coordination have been reported [1].

As part of a systematic study of hypervalent silicon [2], germanium [3], and tin [4] derivatives containing *N*-amidomethyl and *N*-lactamomethyl C,O-chelating ligands, we have shown earlier that the reaction of *N*-trimethylsilyl (*N*-TMS) derivatives of amides and lactams with ClCH₂MMe₂Cl (M = Si, Ge) [5] proceeds through more than one step [6]. NMR monitoring data indicate that the first step is a transmetallation reaction producing Me₃SiCl [6]. In the case of ClCH₂SiMe₂Cl [M = Si], the transmetallation step is rapid, and is complete within a few minutes even at low temperatures (from -60 to -80 °C). When

* Corresponding author.

E-mail address: baukov@rsmu.ru (Y.I. Baukov).

* Deceased July 4, 2004.

the temperature increases ($-30 < T < -20$ °C), the *N*-[chloromethyl(dimethyl)silyl] intermediates (Si analogs of **1**, Si-**1**, Scheme 1) undergo intramolecular *O*-silylmethylation to yield the corresponding *O*-(chlorodimethylsilylmethyl)imides (Si-**2**) which subsequently isomerize to *N*-silylmethylated products (Si-**3**) upon further increase in temperature (up to 0–25 °C). In the case of $\text{ClCH}_2\text{GeMe}_2\text{Cl}$ similar transformations occur under more severe conditions [7]. The formation of the transmetallation intermediates (Ge-**1**) is observed at ~ -20 °C, whereas their transformation into *O*-germylmethylated compounds (Ge-**2**) proceeds between -10 and 10 °C, and the following isomerization into the final *N*-germylmethylated (Ge-**3**) at 60 °C or higher temperatures. Here, we discuss the reactions of chloro(chloromethyl)dimethylstannane with *N*-TMS derivatives of amides and lactams and present the X-ray structure of **3b**. Quantum-mechanical calculations (MP2/LanL2DZ/D95) were employed to study the structure and thermodynamic stability of **3b** as well as its Si- and Ge-analogs.

2. Results and discussion

2.1. Synthesis and NMR studies

The reactions of $\text{ClCH}_2\text{SnMe}_2\text{Cl}$ with *N*-TMS-amides and -lactams require more drastic conditions than those necessary for the silicon and germanium analogs [8].

NMR monitoring of a mixture of equimolar amounts of $\text{ClCH}_2\text{SnMe}_2\text{Cl}$ and *N*-TMS-*N*-methylacetamide in CDCl_3 shows initially only the formation of an intermolecular (1:1) complex of the reactants at -30 to -60 °C, and no noticeable transmetallation product, as is evident from the absence of Me_3SiCl formation. Formation of similar molecular adducts between Me_2SnCl_2 and Me_3SnBr with donor solvents (including DMF) has been reported previously [9a]. The adduct formation is indicated by a large upfield shift of the corresponding ^{119}Sn NMR signal, from 112.3 ppm (in CDCl_3 , characteristic of $\text{ClCH}_2\text{SnMe}_2\text{Cl}$), to -1.5 ppm at 20 °C, assigned to the 1:1 adduct. The latter signal is temperature dependent, -50 ppm at -50 °C. A small amount of the unstable transmetallation product **1a**

($\text{R}^1 = \text{R}^2 = \text{Me}$) appears and is observed in the NMR spectra for 2 h at -20 °C and for 5 min at 20 °C, perhaps as DA-complexes with $\text{ClCH}_2\text{SnMe}_2\text{Cl}$, before reacting further to **2**. The formation of products **2a** and **3a** (in a 2:7 population ratio) is complete at room temperature within 80 h. At 70 °C, the reaction is complete within 5 h and leads to a different product ratio, **2a:3a** = 1:10. The NMR parameters of compounds **1a–3a** are collected in Table 1.

Interestingly, the analogous reactions of $\text{ClCH}_2\text{SnMe}_2\text{Cl}$ with *N*-triethylgermyl- and *N*-trimethylstannyl-*N*-methylacetamides in CDCl_3 solutions were found to proceed faster. NMR monitoring revealed that these reactions are complete within 20–25 min at 60 °C to yield 7:3 and 5:4 ratios of the products **2a:3a** for *N*-germylated and *N*-stannylated amides, respectively.

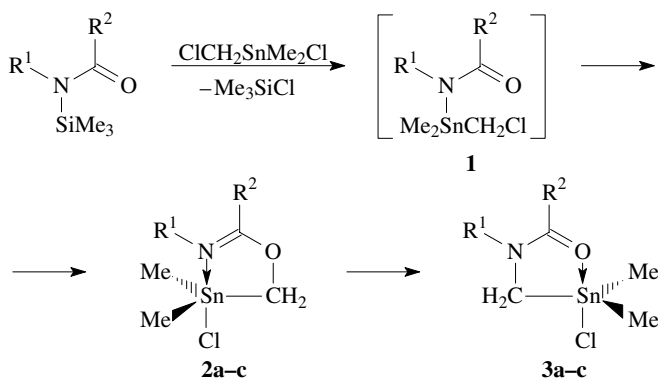
These results suggested a synthetic strategy for the preparation of compounds **2a** and **3a**: the (*N*-Sn)-chelate **2a** was prepared in 62% yield by stirring an equimolar CDCl_3 solution of $\text{ClCH}_2\text{SnMe}_2\text{Cl}$ and *N*-triethylgermyl-*N*-methylacetamide at 20 °C for 48 h, followed by crystallization from *n*-heptane. Heating of a similar solution in *n*-heptane to 100 °C for 24 h, followed by crystallization from ether, afforded the (*O*-Sn)-chelate **3a** as a yellowish amorphous product (m.p. 220 °C), which contained a few percent of the isomeric **2a**.

Preparation of the *N*-lactamomethyl derivatives **3b,c** as individual compounds requires even higher temperatures. Similar to their silicon [6] and germanium [7] analogs, tin derivatives **2b,c** and **3b,c** can be characterized in the IR spectra by the adsorption bands at ~ 1655 (average intensity) of the $\text{C}=\text{N}$ adsorption and ~ 1590 and 1500 cm^{-1} (strong) of the NCO fragment. In the IR spectrum of the solution of *N*-TMS-caprolactam and $\text{ClCH}_2\text{SnMe}_2\text{Cl}$ in an inert solvent (*o*-xylene), both types of these absorptions were found to appear simultaneously at 80–100 °C. Refluxing the reaction mixture (144–145 °C) noticeably increases the absorption at 1590 cm^{-1} , although the band of the lac-

Table 1
 ^1H , ^{13}C , ^{14}N , ^{119}Sn NMR chemical shifts (spin-coupling constants, Hz) of compounds **1a–3a**

Compound		δ (ppm)				
		$(\text{CH}_3)_2\text{Sn}$	CH_3C	CH_3N	SnCH_2	OCN
1a ^a	^1H	0.43	2.04	2.91	3.28	
	^{119}Sn	8.7				
2a	^1H	0.63	2.02	2.93	3.92	
	^{13}C	0.23	15.71	32.94	57.75	171.9
		$^1J_{\text{CSn}}$ 566 Hz			$^1J_{\text{CSn}}$ 632 Hz	
		^{14}N -186.06				
3a	^1H	0.67	2.12	3.22	2.87	
	^{13}C	0.87	20.10	39.11	40.14	174.4
		$^1J_{\text{CSn}}$ 546 Hz			$^1J_{\text{CSn}}$ 552 Hz	
		^{14}N -278.16				
		^{119}Sn -40.60				

^a The ^{14}N chemical shifts are given from CH_3NO_2 .



Scheme 1.

tim ester **2c** (1655 cm^{-1}) still remains the most intensive. Removal of the solvent and heating of the residue in a sealed tube at $170\text{--}180\text{ }^\circ\text{C}$ leads to a fast increase of the absorption at 1590 cm^{-1} , and an appearance of a second band of the amide fragment at 1500 cm^{-1} while the intensity of the band at 1655 cm^{-1} gradually decreases. However, even under such conditions the isomerization **2c** \rightarrow **3c** could not be brought to completion, since further increase in temperature leads to decomposition of the reaction products. Compound **3c** was separated from the reaction mixture in 51% yield by multiple re-crystallizations of the solids from *n*-heptane. An analogous technique was used for the preparation of the δ -valerolactam derivative **3b** in 67% yield.

Compounds **2a** and **3a** can be identified by their different NCO moieties, using ^{14}N NMR spectroscopy. The ^{14}N chemical shifts for **2a** and **3a** are listed in Table 1, and they are in general agreement with ^{14}N and ^{15}N NMR chemical shift data for imide (N=C–O) and amide (N–C=O) compounds, respectively [10]. This further confirms the structure assignments for **2a** and **3a**. The ^{119}Sn NMR chemical shifts for compounds **2** and **3** (**2a**, -73.5 ; **3a**, -40.6 ; **3b**, -42.8 ; and **3c**, -35.3 ppm) provide evidence for the pentacoordination around the tin atom. These resonances are shifted $147\text{--}185$ ppm upfield relative to the tetracoordinate analog $\text{ClCH}_2\text{SnMe}_2\text{Cl}$, and hence are certainly pentacoordinate. The significant chemical shift differences in this series suggests that the extent (or strength) of pentacoordination decreases in the order listed above.

Additional evidence for the hypercoordination is found in the $^1J_{\text{Sn-C}}$ coupling constants of compounds **2a** and **3a** (Table 1). The measured values, which are well above 500 Hz , are characteristic of pentacoordination in tin compounds, and are significantly greater than values reported for tetracoordinate tin compounds ($\sim 400\text{ Hz}$) [1b,11].

The relatively slow transmetalation and following rearrangement observed in the tin compounds, relative to the silicon and germanium analogs, may result from a stronger M–Cl bond, on the one hand, and from the tendency of tin compounds to form molecular adducts with donor molecules, such as the solvents, including amides [9].

2.2. X-ray structural analysis of **3b**

An X-ray diffraction analysis of **3b** reveals a TBP arrangement at the tin center, with the oxygen and halogen atoms in axial positions (Fig. 1). Similar to the silicon and germanium analogs Si-**3b** [12] and Ge-**3b** [13], the chelate cycle in **3b** is nearly planar and the deviations of its atoms from the mean plane are within the limits of $\pm 0.04\text{--}0.06\text{ \AA}$. The favorable twist conformation of the 6-membered lactam ring has an approximate twofold axis passing through the midpoints of the N(1)–C(4) and C(6)–C(7) bonds. However, while in Si-**3b** and Ge-**3b** the deviation from local symmetry is relatively small, with the corresponding torsion angles, C(4)C(5)C(6)C(7) and N(1)C(8)C(7)C(6)

nearly equal (difference smaller than 3°), in structure **3b** this difference reaches 9° . Thus, the conformation of this ring in **3b** may be better defined as a “sofa” with the C(6) atom deviating by 0.65 \AA from the mean plane of the other five atoms (in which the maximum deviation from the plane is $\pm 0.09\text{ \AA}$). Apparently, the increased local-symmetry distortion in **3b** causes a variation in the crystal packing: while Si-**3b** and Ge-**3b** have similar crystal structures (space group $P2_12_12_1$, corresponding unit cell dimensions differ by only $0.04\text{--}0.21\text{ \AA}$), that of **3b** is totally different ($Pbca$). This contrasts with the isomorphism observed in bis-*N*-lactamomethyl derivatives of hexacoordinate Ge and Sn dihalogenides [4,14].

The geometry of the hypervalent OMC_3Cl moiety retains a TBP shape but changes significantly in the Si-**3b** \rightarrow Ge-**3b** \rightarrow **3b** series. Both components of the hypervalent O–M–Cl bond lengthen as the size of the M atom increases, although in different manners (Table 2); the O–M distance increases more significantly (0.227 \AA) upon replacement of silicon by germanium than when germanium is replaced by tin (0.122 \AA). Conversely, the M–Cl bond increases only slightly when Ge replaces Si (Si-**3b** \rightarrow Ge-**3b**, 0.063 \AA) and more significantly (0.126 \AA) when tin replaces Ge. For comparison, ester complex **4**, with the same tin coordination but different C,O-chelate ligand [15] has been included in Table 2, as well as the intermolecular adducts **5** [9d] and **6** [9e] (see Scheme 2).

The variation of **3b** and its Si- and Ge-analogs, Si-**3b** and Ge-**3b** from TBP geometry may be estimated by the deviation of the central atom from the equatorial plane (ΔM ; for ideal TBP $\Delta M = 0$), as well as by the sum of equatorial angles C–M–C (\sum_{eq} ; for ideal TBP $\sum_{\text{eq}} = 360^\circ$). This comparison (Table 2) indicates that the deviation increases in the order $\text{Si} < \text{Ge} < \text{Sn}$.

The extent of deviation of the OMC_3Cl moiety from TBP toward tetrahedral geometry may also be defined by a single parameter $\Delta\Omega = 2\pi - \Omega$, where Ω is the solid angle¹ formed by three equatorial bonds of the M atom [18]. Instead of standard sr or msr ($= 10^{-3}\text{ sr}$) units for Ω , we use more convenient (although non-standard) degree units ($^\circ$) defined as $360^\circ = 2\pi\text{ sr}$. The deviation from the ideal TBP (a planar equatorial environment of the M atom) increases in the series of $\text{Si} < \text{Ge} < \text{Sn}$ (more significantly on the substitution of Si with Ge). Nearly the same differences of $\Delta\Omega$ (ca. 10°) were observed for the Ge and Sn bis-lactam analogs with hexacoordinated M atom [4a],

¹ Solid angle (Ω) can be defined as the ratio of the area cut out by a cone on a sphere that has its center at the cone vertex to the square of the sphere radius. The standard unit for solid angle (steradian, sr) is rather inconvenient for us because of the need to compare, e.g., such values as 0.87 and 1.05 sr while keeping in mind the limit $\pi = 3.14\text{ sr}$ of the Ω deviation ($\Delta\Omega$) from $2\pi = 6.28\text{ sr}$ for ideal trigonal bipyramid. The formal unit “degree of solid angle” $= (1/180)\pi\text{ sr}$ is much more convenient because the maximum value for $\Delta\Omega$ (tetrahedral coordination) is equal to 180° . The solid angle values are given as two-digit numbers, since the typical e.s.d.’s are $\leq 5^\circ$. For the above examples these values are 50° and 60° , respectively.

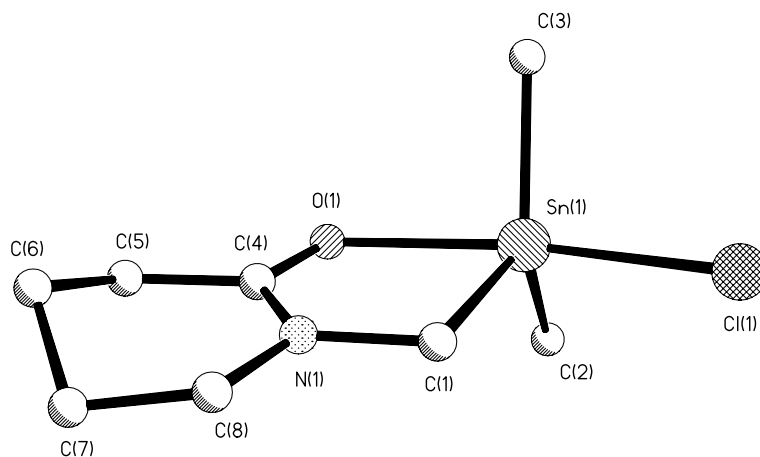


Fig. 1. General view of **3b** in the crystal. Hydrogen atoms are omitted. Important bond lengths (Å) and angles (°): Sn(1)–O(1) 2.303(3), Sn(1)–Cl(1) 2.490(1), O(1)–C(4) 1.254(4), N(1)–C(4) 1.328(5), C(2)–Sn(1)–C(3) 120.8(2), C(2)–Sn(1)–C(1) 116.7(2), C(3)–Sn(1)–C(1) 119.9(2), O(1)–Sn(1)–Cl(1) 167.36(6), C(4)–O(1)–Sn(1) 112.4(2), Cl(1)–Sn(1)–C(1) 92.3(1), Cl(1)–Sn(1)–C(2) 97.4(1), Cl(1)–Sn(1)–C(3) 96.2(1).

Table 2
Selected structural parameters for related TBP (O–M)chelates Si-**3b** [12], Ge-**3b** [13], **3b** and **4** [15] and chlorotriphenylstannane adducts **5** [9d] and **6** [9e]

Compound	M	$d(\text{O–M})$ (Å)	$\Delta d(\text{O–M})$ (%) ^a	$\lambda_{\text{O–M}}$ (%) ^b	$d(\text{M–Cl})$ (Å)	$\Delta d(\text{M–Cl})$ (%) ^a	OMC (°)	$\sum_{\text{eq}}^{\text{c}}$	ΔM (Å) ^d	$\Delta\Omega$ (°) ^e	η_{a} (%) ^f	η_{c} (%) ^f	η_{Ω} (%) ^f
Si- 3b	Si	1.954	19.9	80.1	2.307	12.5	171.1	359.7	0.058	19	91	99	90
Ge- 3b	Ge	2.181	23.9	76.1	2.363	9.9	170.6	358.3	0.147	45	78	95	75
3b	Sn	2.303	18.7	81.3	2.489	5.9	167.4	357.4	0.196	55	73	92	70
4	Sn	2.470	27.3	72.7	2.432	3.5	172.1	352	0.34	90			
5	Sn	2.399	23.7	76.3	2.485	5.7	175.9	357.4	0.20	55			
6	Sn	2.499	28.8	71.2	2.451	4.3	179.2	355.65	0.26	71			

^a Lengthening of bond distance in relation to the single one. Standard lengths of the “tetrahedral” bonds used: $d_{\text{Si–O}} = 1.63$ Å, $d_{\text{Si–Cl}} = 2.05$ Å [16], $d_{\text{Ge–O}} = 1.76$ Å, $d_{\text{Ge–Cl}} = 2.15$ Å, $d_{\text{Sn–O}} = 1.94$ Å, $d_{\text{Sn–Cl}} = 2.35$ Å [17].

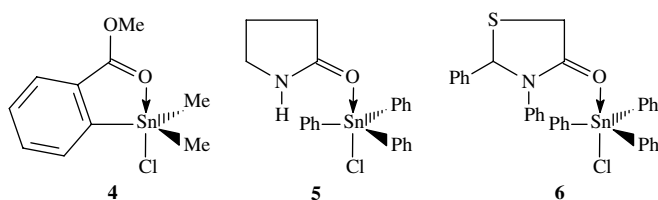
^b $\lambda_{\text{O–M}} = (1 - \Delta d(\text{O–M})/d(\text{O–M})) \times 100\%$, the covalent character of the O–M bond.

^c Sum of equatorial angles.

^d Deviation of the central atom from the equatorial plane toward the halide atom.

^e Ω is a solid angle formed by three equatorial bonds of the central atom, $\Delta\Omega = 2\pi - \Omega$ (0° for ideal TBP and 180° for ideal tetrahedron).

^f Pentacoordination character of the M atom.



Scheme 2.

although the $\Delta\Omega$ values themselves are smaller by ca. 15° in the last case.

Along with the parameters $\eta_{\text{a}} = \frac{109.5 - \frac{1}{3} \sum_{n=1}^3 \theta_n}{109.5 - 90} \times 100\%$ and $\eta_{\text{c}} = 100\% - \frac{120 - (\frac{1}{3} \sum_{n=1}^3 \varphi_n)}{120 - 109.5} \times 100\%$ (where θ_n are the bond angles between the axial and equatorial bonds at the M atom, and φ_n are those between the equatorial bonds) proposed by Tamao et al. [19], the character of TBP pentacoordination of the M atom can be characterized also with the quantity $\eta_{\Omega} = (1 - \frac{2\pi - \Omega}{\pi}) \times 100\%$ ($\Omega = 2\pi$ corresponds to $\eta_{\Omega} = 100\%$; $\eta_{\Omega} = 0\%$ when $\Omega = \pi$). The data from Table 2 reveal that the increase in

size of the central atom M in the ClMC₃O coordinational center in the series of Si–Ge–Sn results in a decrease (sharp, judging by the close values of η_{a} and η_{Ω} , but smooth, judging by η_{c}) of its pentacoordination. The covalent character of the O–M bond changes inconsistently with the η_{a} , η_{c} , η_{Ω} and $\Delta\Omega$ values. Indeed, among structures Si-**3b**, Ge-**3b**, **3b** a maximum $\lambda_{\text{O–M}}$ and minimum η_{a} , η_{c} , η_{Ω} values were found for the (O–Sn)chelate **3b**.

Generally, in organic derivatives of penta- and hexacoordinated Si, Ge and Sn, the near TBP or octahedral coordination shifts from a quasi-mirror symmetry (when the M atom lies in the equatorial plane along the Si → Ge → Sn row). Of course, this trend is clear only if the axial atoms do not vary significantly from a collinear arrangement among the molecules considered.

The data from Table 2 suggest that TBP coordination of the M atom cannot be described accurately by the axial bond lengths because the relations between their increments are different for Si → Ge and Ge → Sn replacement, despite the lengthening of all the O–M bonds versus their “tetrahedral” states are much greater than that of the

M–Cl bonds. On the other hand, the comparison of the derivatives of pentacoordinated tin (**3b**, **4–6**) with similar coordination environment indicates that the equality of the Sn–Cl bond lengths in **3b** and **5** does not mean the same for the opposite O–Sn bonds. However, the $d(\text{Sn–Cl})$ versus $\Delta\Omega$ dependence is monotonic in all these structures (a similar and more complete curve for chlorides of the pentacoordinated Si was obtained by us earlier [20]). On the contrary, the $d(\text{O–Sn})$ values in the intermolecular complexes **5** and **6** exceed the corresponding distances in the (O–Sn) chelates **3b** and **4** by ~ 0.1 Å when the $d(\Delta\Omega)$ values are compared at the same $\Delta\Omega$'s. Analogous feature was found to be characteristic of the TBP silicon compounds [20]. The difference between endo (included in a chelate cycle) and exo states of the C=O group cannot be attributed to steric tension of the chelate cycle because such tension leads to elongation of endocyclic bonds.

Thus, it should be accepted that a type of donating properties of the O atom depend essentially on its inclusion in a chelate cycle.

2.3. Quantum-chemical (MP2/LanL2DZ/D95) study of the structure and the thermodynamic stability of (O–M)chelates of chlorodimethyl(N-amidomethyl)silanes, -germanes, and -stannanes

MP2 calculations with the LanL2DZ (designed for heavy elements, supplemented with polarization functions and relativistic parameterization of the core potential [21,22]) and D95 (Dunning/Huzinaga full double zeta [23]) basis sets demonstrate a significant thermodynamic stability of the (O–M)chelate molecules Si-**3b**, Ge-**3b**, **3b** (M = Si, Ge, Sn) relative to the (N–M)chelate *O*-imydome-ethyl derivatives Si-**2b**, Ge-**2b**, **2b**. Inclusion of zero point vibrational corrections brings the differences in total energies between **3** and **2** to 18.0, 19.3, and 20.2 kcal/mol, respectively, for the compounds of silicon, germanium, and tin. The correspondence of optimized structures Si-**2b**, Ge-**2b**, **2b**, Si-**3b**, Ge-**3b**, and **3b** to the local minima on the potential energy surface (PES) was confirmed by positive eigenvalues of the corresponding Hessians [24].

The results obtained suggest that the different **2:3** product ratios observed by NMR for the silyl, germyl and stan-nyl derivatives (Scheme 1) is dictated solely by kinetic factors, i.e., by increase of the barriers for the Si-**2b** → Si-**3b**, Ge-**2b** → Ge-**3b**, **2b** → **3b** rearrangements with the increase of the M atom size.

The calculations predict that the flat character of the five-membered chelate cycles OCNCM and the “sofa” conformation of the six-membered lactam cycles observed in the crystals of Si-**3b**, Ge-**3b**, and **3b** are retained in the isolated molecules in the gas phase. A large difference between the calculated gas-phase (gas) and the X-ray determined solid phase (solid) structural parameters is characteristic of the internuclear distances O···M (see Tables 2 and 3), and this difference ($\Delta d(\text{O–M})^{\text{gas–solid}} = d(\text{O–M})^{\text{gas}} - d(\text{O–M})^{\text{solid}}$) depends quantitatively on the M atom nature.

Table 3

Some structural parameters and energetics of complexation of (O–M)chelates Si-**3b**, Ge-**3b**, **3b** calculated at the MP2/LanL2DZ level of theory

Compound	Si- 3b	Ge- 3b	3b
$d(\text{O–M})$ (Å)	2.258	2.305	2.338
$\lambda_{\text{O–M}}$ (%) ^a	61.5	69.0	79.5
$d(\text{M–Cl})$ (Å)	2.332	2.386	2.518
$\Delta\Omega$ (°)	57	61	61
η_{a} (%) ^b	71	70	70
η_{c} (%) ^b	91	90	90
η_{Ω} (%) ^b	68	66	66
$\Delta E_{\text{compl}}^{\text{+ZPE}}$ (kcal/mol) ^c	7.2	9.7	15.1
ΔG_{compl} (kcal/mol) ^c	6.0	8.3	13.4

^a Covalent character of the O–M bond (use of the well-known expression for the covalent character of the coordinate bonds χ given by Reed et al. [25] is hampered by the absence of reliable values for the van der Waals radii for the germanium and tin atoms).

^b Pentacoordination character of the M atom.

^c $\Delta E_{\text{compl}}^{\text{+ZPE}}$ and ΔG_{compl} were calculated as a difference of total energies with ZPE corrections and free energies of (O–M)chelate and its open form.

The greatest difference is demonstrated by the O–Si coordination bond, whereas a minimum difference is observed for O–Sn: $\Delta d(\text{O–Si})^{\text{gas–solid}} (\approx 0.30 \text{ Å}) > \Delta d(\text{O–Ge})^{\text{gas–solid}} (\approx 0.11 \text{ Å}) > \Delta d(\text{O–Sn})^{\text{gas–solid}} (\approx 0.03 \text{ Å})$. The stronger axial Cl–M bonds do not respond to the gas → solid transition so dramatically: $\Delta d(\text{Cl–Si})^{\text{gas–solid}} \approx \Delta d(\text{Cl–Ge})^{\text{gas–solid}} (\approx 0.02 \text{ Å}) < \Delta d(\text{Cl–Sn})^{\text{gas–solid}} (\approx 0.03 \text{ Å})$.

Taking into account the inverse character of changes in $\Delta d(\text{O–M})^{\text{gas–solid}}$ and the covalent character ($\lambda_{\text{O–M}}$) of the O···M contact, a decrease in stability of intramolecular complexes Si-**3b**, Ge-**3b**, and **3b** in the series of (O–Si) < (O–Ge) < (O–Sn) should be expected. According to the data in Table 3, this qualitative conclusion is supported by the direct calculation of the total (ΔE_{compl}) and free (ΔG_{compl}) complexation energies.

The calculation results and X-ray data (Tables 2 and 3) suggest that the substitution Si → Ge → Sn results in irregular (unpredictable) character of change in the gas-phase and solid-phase parameters determining the covalent character of the O–M bond ($\lambda_{\text{O–M}}$) and the pentacoordination character of M (η). Their correct use (for example, for the estimation of the complex stability) seems to be possible for a number of reasons only in analyses of structure of chelates with the coordination centers of the same type. Among these reasons is likely to be a dependence of the nonvalent interactions and the force constants of the coordination CIMC₃O center bond angles as well as the effect of the crystal field on the nature of M atom. All calculations were performed using the GAUSSIAN-98 [22] software package.

3. Experimental

The ¹H, ¹³C and ¹¹⁹Sn NMR spectra were obtained on a JEOL FX 90Q (89.5, 22.5, and 33.6 MHz, respectively) and

Varian VXR-400 spectrometers (400.1, 100.6, and 149.2 MHz, respectively). ^{14}N NMR spectra were measured on the former spectrometer at 6.4 MHz. The ^1H and ^{13}C chemical shifts are reported relative to internal Me_4Si . The ^{119}Sn and ^{14}N chemical shifts are reported relative to external Me_4Sn and CH_3NO_2 , respectively.

The syntheses of the initial *N*-trimethylsilyl lactams and *N*-trimethylsilyl-*N*-methylacetamide were reported earlier [26]. *N*-Triethylgermyl- and *N*-trimethylstannyl-*N*-methylacetamide were prepared from sodium derivative of *N*-methylacetamide in THF and Et_3GeBr and Me_3SnBr , respectively. The crude products were used in the reactions with $\text{ClCH}_2\text{SnMe}_2\text{Cl}$ without further purification.

3.1. (*N*-Sn) Chelate *O*-(chlorodimethylstannylmethyl)-*N*-methylisoacetimide (**2a**)

Sodium (2.3 g, 0.1 mol) was suspended in toluene (25 ml) and a solution of *N*-methylacetamide (7.3 g, 0.1 mol) in THF (50 ml) was added. The mixture was heated under argon for 24 h. When all sodium had reacted, triethylbromogermane (23.9 g, 0.1 mol) was added and the mixture was heated for 4 h. The volatiles were removed in vacuo, the residue was distilled and the fraction with b.p. 90–95 °C (1 mm Hg) was collected. The identity and purity of the resulting *N*-triethylgermyl-*N*-methylacetamide were confirmed by ^1H NMR spectrum. A solution of *N*-triethylgermyl-*N*-methylacetamide (0.9 g, 4 mmol) and $\text{ClCH}_2\text{SnMe}_2\text{Cl}$ (0.91 g, 4 mmol) in CHCl_3 (10 ml) was stirred for two days at 20 °C in an evacuated flask. The lower oily layer that formed was separated and added to 20 ml of *n*-heptane. The mixture was kept undisturbed at 20 °C for a day, and the resulting precipitate was filtered, washed with *n*-heptane and dried in vacuo to give 0.64 g (62%) **2a** as a colorless crystalline product. M.p. 176–177 °C. Anal. Calc. for $\text{C}_6\text{H}_{14}\text{NOCISn}$: C, 26.65; H, 5.22; Cl, 13.13; Sn, 43.89. Found: C, 26.25; H, 5.11; Cl, 13.07; Sn, 43.61%.

3.2. (*O*-Sn) Chelate *N*-(chlorodimethylstannylmethyl)-*N*-methylacetamide (**3a**)

A solution of *N*-trimethylsilyl-*N*-methylacetamide (1.93 g, 13 mmol) and $\text{ClCH}_2\text{SnMe}_2\text{Cl}$ (3.1 g, 13 mmol) in 10 ml of *n*-heptane was heated to 100 °C and stirred for 24 h in an evacuated flask. After cooling of the reaction mixture to ambient temperature, the lower oily layer was separated and added to 20 ml of ether. The volatiles were removed in vacuo and the resulting precipitate was isolated by filtration, washed with Et_2O and dried in vacuo to give 2.28 g (68%) **3a** as a yellowish amorphous product, m.p. 220 °C. Anal. Calc. for $\text{C}_6\text{H}_{14}\text{NOCISn}$: C, 26.65; H, 5.22; Cl, 13.13; Sn, 43.89. Found: C, 26.32; H, 5.31; Cl, 13.56; Sn, 43.50%.

3.3. (*O*-Sn) Chelate *N*-(chlorodimethylstannylmethyl)-2-hexahydroazepinone (**3c**)

Method (a): A solution of *N*-TMS-2-hexahydroazepinone (0.95 g, 5 mmol) and $\text{ClCH}_2\text{SnMe}_2\text{Cl}$ (1.17 g, 5 mmol) in *o*-xylene (20 ml) was heated gradually. At 80–100 °C the IR spectrum of the reaction mixture showed two absorption bands at 1655 and 1590 cm^{-1} corresponding to *O*- and *N*-alkylated products, respectively. Refluxing in *o*-xylene (144–145 °C) led to noticeable increase of the absorption at 1590 cm^{-1} . Removal of the solvent in vacuo and heating the residue in a sealed ampoule at 170–180 °C led to a fast increase of the absorption at 1590 cm^{-1} , and to the appearance of a new band at 1500 cm^{-1} . This was accompanied by a simultaneous gradual decrease of the intensity of the band at 1655 cm^{-1} . At 190 °C and higher the products underwent fast decomposition. As a result, *method (b)* was used.

Method (b): A solution of *N*-TMS-2-hexahydroazepinone (2.22 g, 12 mmol) and $\text{ClCH}_2\text{SnMe}_2\text{Cl}$ (2.8 g, 12 mmol) in *o*-xylene (40 ml) was refluxed for 3 h. The solvent was removed in vacuo and the residue was heated in a sealed ampoule at 170–180 °C for 20 min. The products were re-crystallized three times from *n*-heptane to give **3c** (1.9 g, 51%). M.p. 109–110 °C (*n*-heptane). IR (CHCl_3 , ν , cm^{-1}): 1590 (s), 1500 (m). ^1H NMR (CDCl_3 , δ , ppm): 0.69 (s, 6H, SnMe_2); 1.6–1.8 (m, 6H, $(\text{CH}_2)_3$); 2.50 (m, 2H, COCH_2); 2.88 (s, 2H, SnCH_2); 3.55 (m, 2H, NCH_2). ^{119}Sn NMR (CDCl_3 , δ , ppm): –35.3. Anal. Calc. for $\text{C}_9\text{H}_{18}\text{ClINOSn}$: C, 34.82; H, 5.84; N, 4.51. Found: C, 34.62; H, 5.89; N, 4.41%.

3.4. (*O*-Sn) Chelate *N*-(chlorodimethylstannylmethyl)-2-piperidone (**3b**)

The preparation of **3b** is analogous to **3c**. From *N*-TMS-2-piperidone (1.0 g, 6 mmol) and $\text{ClCH}_2\text{SnMe}_2\text{Cl}$ (1.4 g, 6 mmol) in *o*-xylene (15 ml), 1.2 g (67%) of **3b** was obtained. M.p. 64–66 °C (*n*-heptane). IR (CHCl_3 , ν , cm^{-1}): 1605 (s), 1505 (w). ^1H NMR (CDCl_3 , δ , ppm): 0.69 (s, 6H, SnMe_2); 1.7–1.9 (m, 4H, $(\text{CH}_2)_2$); 2.39 (t, 2H, COCH_2); 2.74 (s, 2H, SnCH_2); 3.44 (m, 2H, NCH_2). ^{119}Sn NMR (CDCl_3 , δ , ppm): –42.8. Anal. Calc. for $\text{C}_8\text{H}_{16}\text{ClINOSn}$: C, 32.42; H, 5.44; N, 4.73. Found: C, 32.88; H, 5.89; N, 5.21%.

Crystals suitable for X-ray diffraction study were obtained by spontaneous crystallization of the oily product on standing for 3 weeks.

3.5. X-ray crystal study of **3b**

A Siemens P3/PC diffractometer was used ($\lambda_{\text{Mo K}\alpha}$, graphite monochromator, $\theta/2\theta$ scan, $2\theta_{\text{max}} = 54^\circ$, 2439 measured intensities), $T = 160$ K, orthorhombic, $a = 10.271(3)$ Å, $b = 12.001(4)$ Å, $c = 18.216(6)$ Å, $V = 2245(1)$ Å³, $d_{\text{calc}} = 1.753$ g/cm³, $Z = 8$ ($\text{C}_8\text{H}_{16}\text{ClINOSn}$), space group *Pbca*. The structure was solved by direct methods

and refined by full-matrix least-squares on F^2 in anisotropic approximation for non-hydrogen atoms. Hydrogen atoms were localized by difference synthesis and refined isotropically. Absorption correction ($\mu = 24.7 \text{ cm}^{-1}$) was made by the DIFABS program [27]. The final discrepancy factors are $R_1 = 0.032$, $wR_2 = 0.083$ on 2027 reflections with $[I > 2\sigma(I)]$.

4. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Center, as supplementary publication No. CCDC 255639 for **3b**. Copies of the data may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 1223 336 033; e-mail: data_request@ccdc.cam.ac.uk or www: <http://www.ccdc.cam.ac.uk>).

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