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Articles

Stereochemical Flexibility of Bis(amidomethyl)dichlorogermanes. A Novel Dissociative Mechanism of Ligand Exchange in Neutral Hexacoordinated Bischelate Complexes

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A novel dissociative mechanism of (L,L)-ligand-site exchange in neutral hexacoordinated *cis*-($M \leftarrow O$) complexes of the type L_2MX_2 (M = Ge and Sn; X = Hal) is proposed. All the activation parameters of enantiomerization for (C,O)-chelate bis(amidomethyl)dichlorogermanes **4**−**6** have been determined by the dynamic NMR method. The fairly positive values of entropy for exchange in **4**−**6** (up to 17 $\text{cal}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$) suggest an interconversion of chelate ligands followed by a dissociative−associative mechanism. The correlation of activation barriers $\Delta G^{\ddagger}_{298}$ in hexacoordinate L_2GeCl_2 species (**4**−**6**) with intramolecular $Ge \leftarrow O$ distances in the crystals of analogous pentacoordinate $LGeMe_2Cl$ complexes with the same chelate ligand was found. A two-step process for intramolecular exchange including the dissociation of the coordinate $Ge \leftarrow O$ bond and pseudorotation in a pentacoordinate intermediate is considered as a model for the enantiomerization. It is shown that the main factor controlling the stereodynamic process in dichalogermanes **1**−**8** is pseudorotation $\mathbf{B} \leftrightarrows \mathbf{B}^*$ for the pentacoordinate intermediate, while in the analogous tin complexes **9**−**12** it is the $Sn \leftarrow O$ bond rupture $\mathbf{A} \leftrightarrows \mathbf{B}$ in the primary hexacoordinate state.

Introduction

Many neutral complexes of the group 14 elements in which the central atom is hexacoordinated due to intermolecular or intramolecular coordination have been described. A number of the following types of adducts, mainly $X_4M\cdot D_2$ (M = Si,[1] Ge,[2] Sn[2a−c,3]) and $X_2R_2Sn\cdot D_2$,[3a−e,4] were isolated and characterized by means of X-ray crystallography. However, only a few publications[5] deal with *cis/trans*-isomerism around the metal atom in solution of these types of intermolecular complexes because ligand exchange is generally fast on the NMR time scale. In contrast, the stereoisomerization of hexacoordinated intramolecular complexes L_2MXY (M = Si, Ge, and Sn) containing generally two identical bidentate ligands L is a remarkably general phenomenon due to their significantly greater stability by chelate effect,[6] which decreases with increasing the saturated ring size: five-membered structures are more stable than the corresponding six- or seven-membered rings.[7] The stability of the group 14 complexes usually increases in the sequence Si < Ge < Sn.[8]

Accumulated X-ray results on bischelate L_2MXY structures of the group 14 elements indicate that octahedral coordination geometry generally can adopt either a *cis*- or *trans*-configuration for two coordinating

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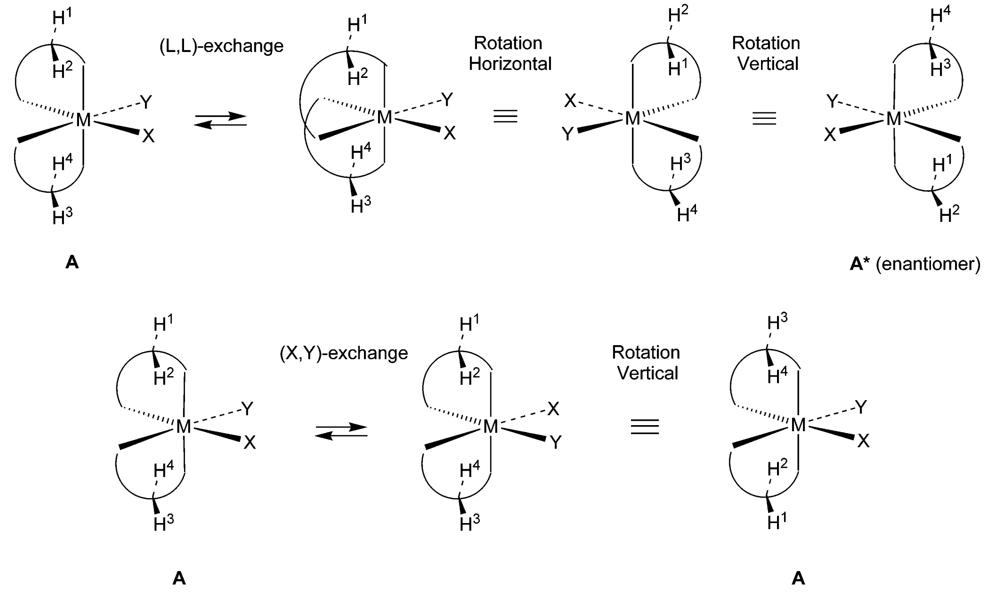

Figure 1. Intramolecular ligand-site (L,L)- and (X,Y)-exchange for hexacoordinated bischelate L_2MXY complexes with *cis*-orientation of two monodentate ligands.

atoms.[1–4] The *cis*/*trans* energy differences are small in these systems, and by a suitable choice of chelating ligands and/or monodentate substituents, it is possible to favor one geometrical isomer over the other and even to allow the isolation of both forms.[5j,9] In solution the hexacoordinate complexes L_2MXY undergo ligand exchange processes, which are caused by epimerization and/or enantiomerization. In the case of X = Y, an element of chirality may be realized by an enantiomeric arrangement of the identical chelate ligands about the metal.[10]

The CH_2 groups usually presented in chelate ligands are appropriate for studying dynamic NMR spectra because prochiral methylene protons may interconvert and display typical coalescence phenomena. For L_2MXY complexes with the *cis*-MXY moiety, two intramolecular (L,L)- and (X,Y)-exchanges of the adjacent ligands (1,2-shift) may be considered (Figure 1). In the absence of ligand exchange, the methylene protons display an AB spin system corresponding to the diastereotopic protons CH^1H^2 and CH^3H^4. The (L,L)-exchange is an interchange of chelate ligands between the two enantiomers and accounts for the coalescence of ($H^1 \rightleftarrows H^4$) and ($H^2 \rightleftarrows H^3$) protons having a *cis*-orientation relative to each other, while the (X,Y)-exchange does not invert the configuration at the element and brings about coalescence of *trans*-protons ($H^1 \rightleftarrows H^3$) and ($H^2 \rightleftarrows H^4$) for the same diastereomer (Figure 1). The conclusions about the stereodynamic behavior of molecules have been deduced

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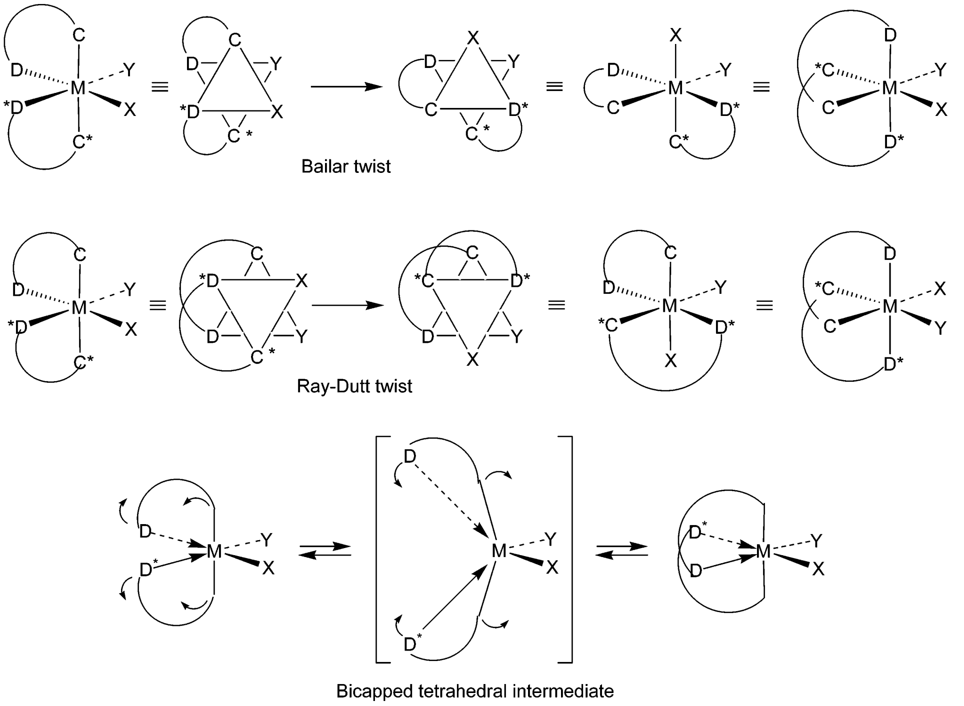
Scheme 1. Stereoisomerization of Hexacoordinated Bischelates L_2MXY through the "Bailar Twist", "Ray−Dutt Twist", and the Formation of a "Bicapped Tetrahedral" Transition State



as a rule on the basis of line shape analysis of the temperature-dependent ^{1}H NMR resonance.[11]

The many possible mechanisms for ligand-site exchange in molecules may be divided in two groups: nondissociation (regular) and dissociation−recombination (irregular). Both the various models for interconversion between isomers in neutral hexacoordinated bischelate species and detailed discussions of the influence of mono- and bidentate ligands on the activation barrier for dynamic processes have been developed and reported for hypervalent 12-M-6 species[12] containing 12 formally assignable electrons at the central atom of group 14 (see below), 15,[13] and 16[14] elements. The simple intramolecular ligand exchange processes participating directly in nondissociative mechanisms are well known as the Bailar twist[15] and the Ray and Dutt twist[16] (Scheme 1), when one triangular face of the octahedron twists relative to the opposite face. In fact, the final structures for the Bailar and Ray−Dutt twist mechanisms (Scheme 1) correspond to the octahedral species for intramolecular (X,Y)-exchange in hexacoordinated bischelate complexes with *trans*-configuration for the two coordinating D atoms. These processes are not often sufficient to account for observations of the dynamic NMR spectra, and a more complicated mechanism involving a "bicapped tetrahedral" transition state (Scheme 1) has also been proposed.[17]

For the latter mechanism, the covalently bonded chelate ligands change locations by twisting out of the plane formed by the axial bonds and placed in the middle of the *cis*-MXY moiety, while the donor atoms D are pushed out from this plane (Scheme 1). The general theoretical studies of rearrangement mechanisms through bicapped tetrahedral intermediates in six-coordinate complexes of transition metals are well known.[18] Perhaps this ground-state structure for the neutral hexacoordinate group 14 elements has been identified in dihydrosilane $(ArO)_2SiH_2$, where ArO = 2,4,6-$[(CH_3)_2NCH_2]_3C_6H_2O$, and the Si←N bond distances of 2.986 and 2.630 Å[19] are somewhat shorter compared with the sum of the van der Waals radii (3.54 Å[20]). However, the six-membered chelate rings arising from Si←N interaction are more strained than that of

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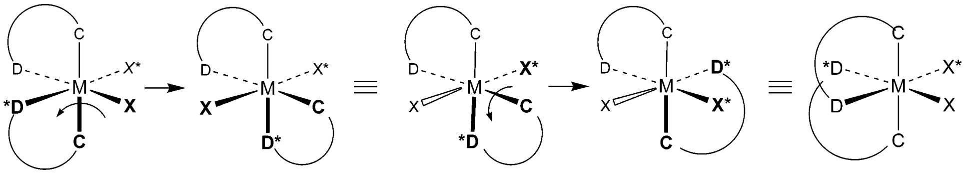
Scheme 2. Proposed Regular Mechanism of the Enantiomerization in Hexacoordinate Germanium Dibromides 7(a−c) and 8 through Two Consecutive Twists[27b]



five-membered ones.[7] Moreover, this type of compound, are also called "pincer complexes" when one chelate ligand has two symmetrical donor atoms that are potentially capable of intramolecular coordination, are usually accompanied by predominant formation of relatively weak intramolecular interaction for main group elements[21] in contrast to transition metals.[7d] Probably for these reasons, for example, in crystals of *N*-(trifluorosilylmethyl)phthalimide the Si←O bond distance of 2.654 Å is longest in comparison with those for other pentacoordinate (C,O)-chelate trifluorosilanes.[22] Dynamic coordination−decoordination processes for such "flip-flop" type complexes reported for silicon[23] and tin[23d,24] derivatives are usually too fast to be observed by NMR, suggesting that the conformationally flexible bridging framework produces an unfavorable entropy of coordination.

The symmetrically substituted *cis*-coordinated bischelate germanium difluorides **1**−**3**,[25] dichlorides **4**−**6**,[26] and dibromides **7** and **8**,[27] as well as their tin analogues **9**−**12**,[28] have no chiral center, but get an element of chirality by virtue of an enantiomeric arrangement of ligands about the metal. In a solution of these derivatives, a dynamic equilibrium including ligand-site exchange is observed, and fluxional processes were discussed with respect to the analysis of various types of possible mechanisms.[27b,29] However, it remains to be determined whether the mechanism of the enantiomerization is due to the Ge←O bond rupture or not.[27b,29]

The solid-state structures of germanium dichlorides **4**−**6** (as well as analogous complexes of germanium **1**−**3**, **7**, **8** and tin **9**−**12**) generally have a *cis*-orientation of two Ge←O coordination bonds and the Ge atom adopts a distorted octahedral geometry with the two carbon atoms in *trans*-positions (159.8−167.1°).[26a,30] In two nearly linear Cl−Ge←O fragments (170.6−175.0°) the Ge←O distances (2.09−2.24 Å) are longer than that of the sum of covalent radii (1.925 Å)[31] and essentially less than the sum of van der Waals radii (3.67 Å).[20,32] In contrast to dichlorogermanes **4**−**6**, containing only one *cis*-diastereomer in solution, the NMR spectra of analogous lactamomethyl and amidomethyl dibromides (**7** and **8**) reveal the simultaneous existence of two diastereomers with *cis*- and *trans*-orientation of the Br atoms (and the Ge←O bonds too), which may be caused by the sterically overcrowded *cis*-$GeBr_2$ group, where the Br−Ge−Br angles in **7** are 96.2° (**a**), 95.1° (**b**), and 96.4° (**c**).[27a] The presence of a geminal interaction for Br atoms in the germanium coordination sphere[33] probably excludes the existence of the hexacoordinate dianion $GeBr_6^{2-}$ [34] compared with the known $GeCl_6^{2-}$.[35]

For dibromide complexes **7** and **8**, an exchange between the *cis*/*trans*-diastereomers takes place at higher temperatures ($\Delta G^{\ddagger} = 15-16$ kcal·mol^{-1}), while enantiomerization is observed in the *cis*-diastereomers at lower temperatures ($\Delta G^{\ddagger} = 10-12$ kcal·mol^{-1}).[27b] On the basis of the dependence of the activation energy for *cis*-diastereomers on the Ge←O bond length, a regular nondissociative mechanism of enantiomerization involving the formation of a neutral bicapped intermediate was anticipated.[27b] At the same time, the authors suggest that the alternative twist mechanism may not be excluded (Scheme 2). Taking into account an extremely short intramolecular Ge←O distance and a significant lengthening of the Ge−Br bond of two linear Br−Ge←O fragments in the crystal state, it was pro-

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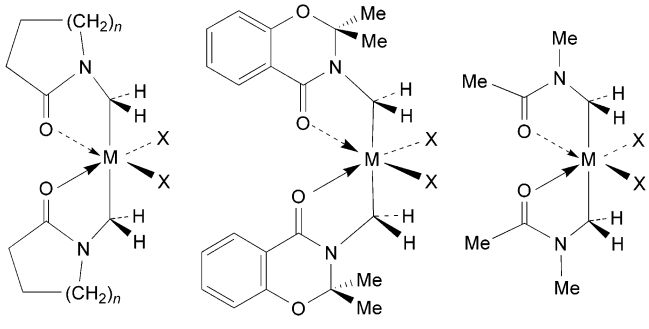
Chart 1



n = 1 (**a**), 2 (**b**), 3 (**c**)

	M, X
(**1**)	Ge, F
(**4**)	Ge, Cl
(**7**)	Ge, Br
(**9**)	Sn, Cl
(**11**)	Sn, Br
(**12**)	Sn, I

	M, X
(**2**)	Ge, F
(**5**)	Ge, Cl

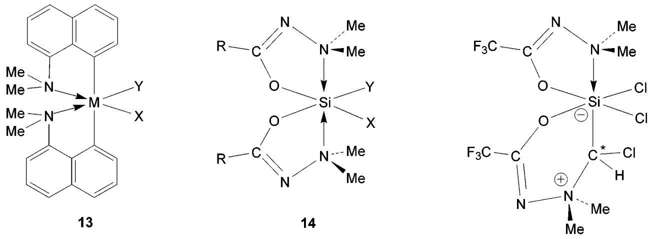
	M, X
(**3**)	Ge, F
(**6**)	Ge, Cl
(**8**)	Ge, Br
(**10**)	Sn, Cl

posed that the epimerization process proceeds via the Ge−Br bond rupture.[27b]

In the tin complexes **9**(**a**−**c**) and **11**(**a**−**c**), the larger vicinal tin coupling constants for the cyclic methylene carbons, $^3J(^{119}Sn-C-N-^{13}CH_2) = 82.2-99.3$ Hz, than for the carbonyl groups, $^3J(^{119}Sn-C-N-^{13}CO) = 21.4-29.7$ Hz, and the absence of $^3J(^{119}Sn\leftarrow O{=}C-^{13}C)$ coupling, were suggested to originate from a direct coupling pathway through the covalent Sn−C−N−C bonds, while the contribution through the coordination bond is very weak or even absent.[28b,36] Consequently, the observation of coupling constants between the tin and the carbonyl group is not in contrast to ligand-site exchange processes involving the dissociation of the coordinate bond in tin complexes **9** and **11**.

In nonsymmetrically substituted silicon (C,N)-bischelate *cis*-complexes **13a** (X, Y = H, F, OMe, Me, Ph) the four *N*-methyl signals coalesce at high temperature to two signals (the free energy of activation for ligand exchange covers a range of 9.3−20.5 kcal·mol^{-1}); that is, the geminal *N*-methyl groups remained diastereotopic, while naphthyl groups become equivalent.[17a,b] This fact was interpreted as a result of an intramolecular nondissociative exchange attributed to one of the twist mechanisms, Bailar or Ray−Dutt. The barrier for the coalescence of the *N*-methyl signals to a singlet in symmetrical tris-chelate **13a** (XY = 1,2-$O_2C_6H_4$) has been obtained as 20.5 kcal·mol^{-1}, but it was not possible to answer the question whether the barrier was due to $Si\leftarrow N$ bond cleavage or not.[17b,37] The ^1H NMR spectra of disilanes **13a** (X = $SiMe_3$, Y = F and OC_2H_5) at room temperature show four broad singlets, indicating the strong enough coordination of the amino groups to silicon to prevent exchange. At the same time, only two singlets were observed for disilanes **13a** (X = $SiMe_3$, Y = H and OH), but the exchange mechanism is not discussed.[38]

Chart 2



13

M = Si (**a**), Sn (**b**)

14

(**a**) X = Cl, Y = Ph,
(**b**) X = Cl, Y = cyclohexyl, R = CF_3
(**c**) X = Y = F, R = Ph
(**d**) X = Y = F, R = CF_3
(**e**) XY = o-C_6H_4, R = Ph
(**f**) XY = o-C_6H_4, R = CH(Me)Ph

15

The mechanisms of intramolecular exchange in silicon (O,N)-bischelate *trans*-complexes **14** (X = F, Cl, Y = H, Me, Ph), whether dissociative or nondissociative, were disputed by I. Kalikhman, D. Kost, and co-workers.[1o,17c,39] Since $Si\leftarrow N$ bond cleavage and the resulting exchange of geminal *N*-methyls in **14a** (R = CH_2Ph) are not accompanied by an exchange of the geminal methylene protons, it was concluded[39a−c] that a nondissociative intramolecular ligand exchange can take place. As a Bailar or Ray−Dutt twist cannot be completely ruled out on the basis of available data, the authors propose that a likely mechanism that accounts for all of the dynamic NMR data is a 1,2-shift of adjacent monodentate ligands or the two oxygen ligands, via a "bicapped tetrahedral" transition state. Taking into account the formation of the siliconium ion salts of chlorosilane **14a** (R = CH_2Ph) in polar nonaqueous solvents at low temperatures, the authors suggest that an ionization of the Si−Cl bond may be considered too.[39h−k] For **14b**, the increasing of both the size of the monodentate ligand at silicon (Y = cyclohexyl leads to steric hindrance for dative bonding) and the electron-withdrawing effect of the substituent (R = CF_3 leads to a decrease in the electron density on the central silicon atom and prevents ionization of the Si−Cl bond) allows the observation of the neutral equilibrium dissociation of a dative bond in the hexacoordinate silicon complex.[39k]

Theoretical calculations of the total electronic energy density and kinetic energy density at the donating nitrogen atom toward the silicon atom in symmetrical

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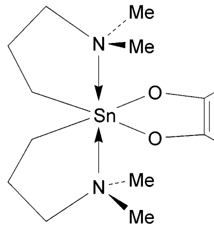
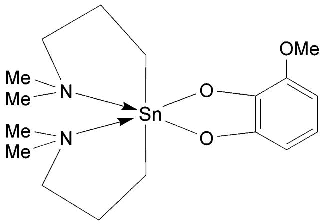
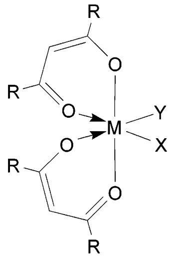
Chart 3



16



17



18

14c suggest predominantly an ionic Si←N interaction and much less hypervalent contribution than commonly anticipated for such bonding.[39o] However, in **14d** the investigation of long fluoro coupling constants, $^3J(^{19}F-Si\leftarrow N-^{13}C)$ and $^4J(^{19}F-Si\leftarrow N-C-^1H)$, through the intramolecular coordination revealed the silicon dative Si←N bond behaves in full analogy with normal covalent bonds.

For symmetrically hexacoordinated silicon tris-chelate **14e**, only one *N*-methyl exchange barrier ($\Delta G^\ddagger = 20.8$ kcal·mol^{-1}) was observed.[39f] The authors believe that relatively low entropy ($\Delta S^\ddagger = 5.4$ cal·mol^{-1}·K^{-1}) of the process is in accord with an intramolecular exchange due to dissociation of the Si←N bond, followed by inversion of the nitrogen and exchange of the hydrazide chelate oxygens via a (O,O)-shift. The presence of the chiral carbon centers in **14f** distinguishes two consecutive exchanges; the lower barrier process is assigned to the (O,O)-shift, and the higher one to the Si←N dissociation.[39f]

One of the diastereomers **15** with the chiral carbon center adjacent to the silicon atom undergoes two intramolecular ligand-site exchange processes: reversible dissociation of the dative Si←N bond ($\Delta G^\ddagger = 16{,}7$ kcal·mol^{-1}) and inversion of configuration at the silicon center ($\Delta G^\ddagger = 21.0$ kcal·mol^{-1}).[39g,n] According to the authors, the relatively higher barrier most likely represents the exchange of adjacent ligands via a "bicapped tetrahedral" transition state.[39g,n]

Octahedral tin complexes containing two bidentate (C,N)-chelating ligands have been well known as typical compounds with a rather strong Sn←N coordination, mainly due to systematic investigations by Jastrzebski, van Koten, and co-workers,[3b,9a,40] as well as Jurkschat, Willem, and co-workers.[41]

The NMR spectra of hexacoordinated bischelate tin complexes **13b** (X, Y = Cl, I, Br, Me, Ph) revealed the existence of two sets of signals corresponding to diastereomers with both *cis*-donor (*trans*-R) and all-*cis*-arrangement,[9a] and at higher temperatures an interconversion process becomes fast on the NMR time scale. The observation of the splitting due to vicinal coupling constants $^3J(^{119}Sn\leftarrow N-C-^1H)$ through the coordinate interaction was considered as evidence for the nondissociative intramolecular process involving the Bailar twist mechanism. However, most recently it has been shown that the use of these constants for the purpose of observing intramolecular donor−acceptor interactions in tin complexes should be viewed with some caution, because the six-bonds coupling 6J(1H-119Sn) through an organic carbon chain was observed for hexacoordinated bis[3-(dimethylamino)propyl]tin derivatives, as well as for model tetracoordinated tin compounds.[42]

X-ray analyses of the hexacoordinated diorganotin compounds **16** and **17** show the distorted-octahedral geometries for the tin atom with *trans*-donor (*cis*-R) and *cis*-donor (*trans*-R) configuration, respectively. It was concluded that the exchange process involves intramolecular Sn←N dissociation with a following enantiomerization by a Berry pseudorotation for pentacoordinate species.[41a] For hexacoordinated bischelate complexes $[Me_2N(CH_2)_3]_2SnF_2$ the loss of the coupling $^1J(^{119}Sn-^{19}F)$ at high temperature during the *cis/trans*-isomerization was accounted for by a dissociative mechanism involving tin−fluorine bond rupture.[9c,41b,43] This was deduced from the observation of $^3J(^{119}Sn\leftarrow N-C-^1H)$ coupling constants for two *N*-methyl groups, whereas such interaction is absent for the NCH_2 protons. However, it was recognized that great care should be taken in using the long coupling constants as indicators of intramolecular donor−acceptor bonding in this complex, since nonzero values of $^6J(^{117}Sn-^1H)$ through covalent bonds are also observed for compounds where coordination interactions are impossible.[42]

Both the dissociation and nondissociation mechanisms of the intramolecular exchange process in the series of acetylacetonates **18** (M = Si, Ge, Sn, X = Cl, Y = Ph, R = Me) and some other similar compounds of tin bearing six-membered (O,O)-chelate ligands have been discussed.[41c,d,44]

The negative entropy of activation $\Delta S^\ddagger = -4.6$ cal·mol^{-1}·K^{-1} was observed for enantiomerization in the hexacoordinated *cis*-bis[(*N*-methylacetamido)methyl]-dibromogermane **8**.[27b] The positive value of $\Delta S^\ddagger = 5.4$ cal·mol^{-1}·K^{-1} was obtained for intramolecular processes in neutral hexacoordinated silicon tris-chelate **14e**.[39f] The values of the entropy for both complexes were discussed in terms of two possible mechanisms including the interconversion of chelate ligands via regular nondissociative exchange and dissociation−recombination of the coordinate bond.

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Table 1. Activation Parameters for the Ligand-Site Exchange in Complexes 4−6

compound	solvent	$\Delta G^{\ddagger}_{298}$ (kcal·mol^{-1})	$\Delta H^{\ddagger}$ (kcal·mol^{-1})	$\Delta S^{\ddagger}$ (cal·mol^{-1}·K^{-1})	d(Ge^{VI}←O),[a] average (Å)	d(Ge^{V}←O)[b] (Å)
4a	$CDCl_3$	10.0 ± 0.3	12.2 ± 0.3	7.3 ± 1.2	2.211[26a]	2.311[48]
	$(CD_3)_2CO$	10.2 ± 0.2	12.0 ± 0.2	6.2 ± 0.9		
4b	$CDCl_3$	12.3 ± 0.2	16.9 ± 0.2	15.3 ± 0.7	2.146[26a]	2.181[49]
	CD_3CN	12.7 ± 0.3	16.2 ± 0.3	11.4 ± 1.2		
	$(CD_3)_2CO$	12.2 ± 0.3	16.8 ± 0.3	15.5 ± 0.9		
4c	$CDCl_3$	12.3 ± 0.2	16.9 ± 0.2	15.3 ± 0.7	2.125[26a]	2.194[50]
	$CDCl_3$[c]	12.4 ± 0.3	17.0 ± 0.3	15.5 ± 1.1		
	CD_3CN	12.6 ± 0.3	16.0 ± 0.3	11.5 ± 1.1		
	$(CD_3)_2CO$	12.3 ± 0.3	16.8 ± 0.3	15.2 ± 0.9		
	$C_6D_5CD_3$	12.3 ± 0.6	17.2 ± 0.6	16.6 ± 2.0		
5	$CDCl_3$	13.6 ± 0.3	14.9 ± 0.3	4.5 ± 1.2	2.121[51]	
6	$CDCl_3$	12.0 ± 0.3	15.0 ± 0.3	10.0 ± 0.8	2.110[26b]	2.203[d]
	CD_3CN	11.8 ± 0.3	16.7 ± 0.3	16.5 ± 0.8		
	$(CD_3)_2CO$	11.9 ± 0.3	17.0 ± 0.3	17.2 ± 1.1		

[a] The average Ge←O distances in the crystal structure of six-coordinated bischelates **4−6** (L_2GeCl_2). [b] The Ge←O distances in the crystal structure of five-coordinated chelates $LGeMe_2Cl$ with the same ligand. [c] Concentration is about 10 times enhanced. [d] For **6** with NCH(Me)Ph.[52]

Thus, the mechanisms of ligand-site exchange in neutral hexacoordinated bischelate complexes of the group 14 elements appear to be more diverse than usually anticipated. Despite the extensive experimental evidence for the fluxional processes in solution, there are doubts concerning the detailed interpretation of the isomerization up to date. Different types of exchange processes may operate in the molecules, but it often remained to understand which of the various mechanisms really controls the dynamic process.

One fundamental question about the pathway of the ligand-exchange process is whether coordinate bond rupture occurs or not. The next question is whether there is an intermediate, that is, whether the pathway is multistage or not. Unequivocal proof of the mechanism is often neither simple nor straightforward because much of the evidence, based on the free energies of activation at coalescence temperature, is by its nature ambiguous.

Results and Discussion

The earlier data on ligand-site exchange (enantiomerization) processes in **4−6**[29] were ascribed mainly to the detailed discussion of the free energies of activation at coalescence temperature $\Delta G^{\ddagger}(T_c)$. This study has focused on all activation parameters (free energy of activation $\Delta G^{\ddagger}_{298}$, enthalpy $\Delta H^{\ddagger}$, and entropy $\Delta S^{\ddagger}$) for the dynamic behavior of these germanium complexes. Full line shape analysis of the methylene NCH_2 protons in **4−6** has been determined by the DNMR method based on the Bloch equation modified for a chemical exchange.[45] All the activation parameters are given in Table 1. For preliminary results for hexacoordinated (C,O)-chelate bis(2-oxo-1-hexahydroazepinylmethyl)dichlorogermane **4c** see ref 46.

At room temperatures only one set of signals for the germanium complexes **4−6** was detected in the NMR spectra. At low temperatures (below −50 °C), no splitting of the ^{13}C resonance signals occurs for bischelate ligands in **4−6** (C_2 symmetry), with the only exception of methyl groups in **5** ($\delta^{13}C = 25.2$ and 24.3 ppm, $CDCl_3$, −45 °C). However, the NCH_2 protons within each methylene group are diastereotopic and displayed an AB spin system due to molecular chirality. An increase of temperature restores the original spectrum.

It has been known that the free activation energy for silicon complexes **14e** in apolar solvents is higher by 2 kcal·mol^{-1} compared to the polar ones.[1o] In contrast no influence of solvent on the activation barrier for germanium complexes **4c** has been obtained (Table 1).

It has been shown by us that an alternative inversion process for the seven-membered lactam ring in *N*-(chlorodimethylgermylmethyl)hexahydroazepin-2-ones occurs at lower temperature, $\Delta G^{\ddagger}(194) = 9.4$ kcal·mol^{-1}.[53] Further broadening for all methylene protons of **4c** in a mixture of $CDCl_3$ and CD_2Cl_2 (1:1) or $C_6D_5CD_3$ caused by lactam ring inversion was observed at temperatures below 210 K.

No concentration dependence was observed in an interval from 0.2 to 2 M, which excludes the intermolecular mechanism of rearrangement in hexacoordinate dichlorogermanes **4−6**. An intramolecular exchange process through Ge−Cl bond dissociation seems to be unfavorable in view of substantially lower electroconductivities of their solutions in chloroform (40−260 mS·cm^2·mol^{-1}) in comparison with the cation−anion complex with the triflate group $L_2Ge(Cl)OTf$ (1000−2000 mS·cm^2·mol^{-1}).[54] In the present study we have measured the effect of added chloride ion. It has also been found that at room temperature there is no

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influence on the exchange rate in **4**−**6** of the addition of dry nucleophile LiCl or Et$_3$NCH$_2$PhCl (from 0.05 to 0.2 M), indicating the absence of halide dissociation. At the same time, the ionization of the Si−Cl bond in neutral hexacoordinate complexes of silicon **14a** is characterized, despite the increase in number of particles, by the negative entropies of $\Delta S^\circ = -21.8$ (R = *t*-Bu), −15.0 (Me), −9.4 (CH$_2$Ph), and −8.6 cal·mol^{-1}·K^{-1} (Ph) due to stabilization of the ions by solvent organization, which constitutes higher order (and hence negative entropy).[39i]

The relatively high positive entropy of activation in **4**−**6** (Table 1) is in accord with a lot of degrees of freedom for the transition state (smaller ordered species) in comparison with the primary state,[55] which may be explained by rupture of the coordination Ge←O bond, forming a pentacoordinate species. It should be noted that a nondissociative mechanism involving the exchange process, for example, through a trigonal-prismatic transition state, characterizes negative entropy of activation[18a] and could be ruled out.

Thus, the exchange of methylene protons in **4**−**6** must have resulted from a pentacoordinate transition state with evidently an achiral germanium center.[46] We propose a novel (L,L)-exchange mechanism between two enantiomers of hexacoordinated bischelate complexes L$_2$MX$_2$, including the dissociation of the coordinate bond followed by formation of a pentacoordinate species, exchange of ligand positions in a trigonal bipyramidal intermediate, and reclosure of the uncoordinated chelate ligand (Figure 2).

The dissociation of the Ge←O bond in hexacoordinate species **A** (the first step) leads to the formation of neutral pentacoordinate germanium structure **B**. The numerous examples of extra-coordinate germanium complexes in the solution and solid states[2a] suggest that the energies associated with the conversion of six- to five-coordinate species to be small, such that the formation of a pentacoordinate intermediate in the transition state becomes a likely possibility. According to X-ray data for stable trigonal-bipyramidal polyhedra of the germanium (as other group 14 elements), the axial position in a hypervalent X−Ge←O bonding is normally occupied by the most electronegative substituent,[1a,2a] that is, atom Cl in the case of complexes **4**−**6**. [According to Gillespie,[56] the "concept of hypervalence has ceased to be of any practical use" and "there is no reason to regard hypervalent molecules as belonging to a special class". However, the simple and visible assumption of three-center four-electron[57] or hypervalent[58] bonding modified with reference to the group 14 elements[59] is a practically very constructive and useful model that could qualitatively explain and predict the trends observed in the physical-chemical properties of extra-coordinate complexes.[59a,60]] Thus, the transition from six-coordinate **A** to five-coordinate **B** structure (process **A** → **B**) includes the change *only* between the three covalent bonds in the germanium polyhedron (two Ge−C and one Ge−Cl*), while the last hypervalent Cl−Ge←O bonding remains unchanged. Since the Ge←O dissociation followed by rotation about the Ge−C bond alone and subsequent recombination does not lead to equivalence for the geminal protons, the exchange may be achieved only by exchange of monodentate ligands in the trigonal bipyramidal intermediate (process **B** → **B***). The inversion of configuration at germanium through intramolecular **B** → **B*** exchange (the second step) takes place most likely by a pseudorotation mechanism. The recombination of the coordination bond (process **B*** → **C**) results in hexacoordinate structure **C**, which is the enantiomer **A*** of the primary species **A**.

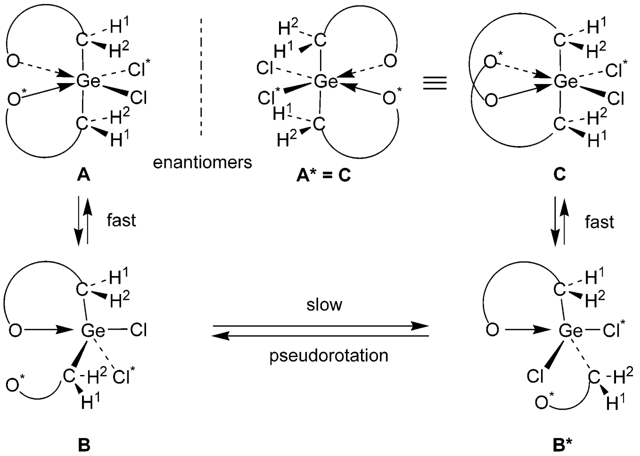

Figure 2. Intramolecular dissociative mechanism of two-step (L,L)-ligand-site exchange (enantiomerization) in neutral hexacoordinated bischelate complexes **4**(**a**−**c**)−**6** through the formation of a neutral pentacoordinate intermediate and subsequent pseudorotation.

The two possible alternative exchange pathways for the replacement of electronegative chlorine atoms in **4**−**6** involve the pseudorotation Berry[61a] or the turnstile mechanism.[61] Inversion of configuration at the pentacoordinate germanium center by Berry pseudorotation must involve a two-step exchange with the only mono-

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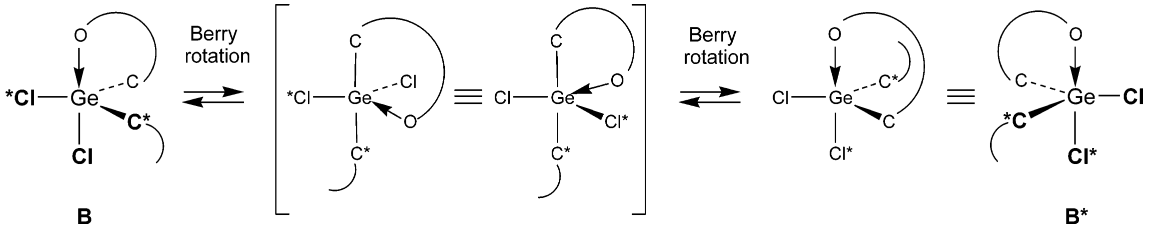

Figure 3. Possible mechanism of intramolecular ligand exchange (**B** ⇆ **B*** process) via two-step Berry pseudorotation.

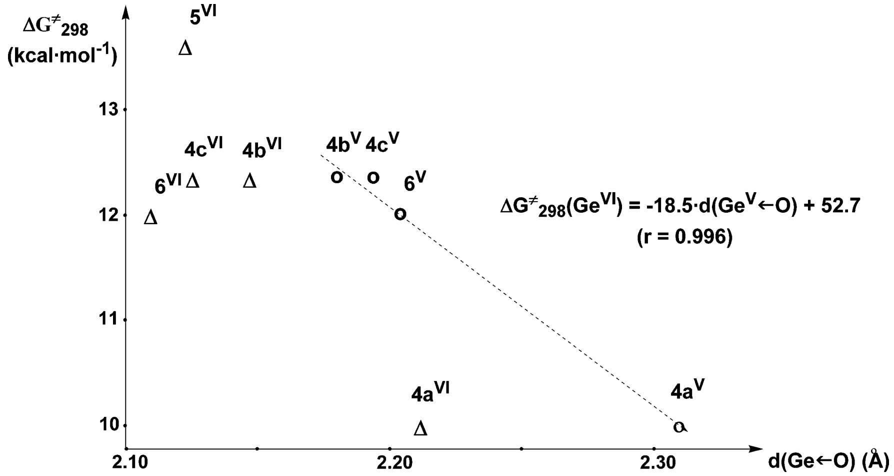

Figure 4. Plot of free energy of activation $\Delta G^{\ddagger}_{298}$($CDCl_3$) of the enantiomerization in **4**–**6** against intramolecular d(Ge←O) distances in the crystals of hexacoordinated bischelates $\mathbf{4^{VI}}$–$\mathbf{6^{VI}}$ (△, $L_2Ge^{VI}Cl_2$ type complexes) and pentacoordinated monochelates $\mathbf{4^{V}}$ and $\mathbf{6^{V}}$ with the same chelate ligand (○, $LGe^{V}Me_2Cl$).

dentate substituent as the "pivot" ligand (Figure 3). This process is intermediate (halfway between two idealized five-coordinate geometries **B** and **B***) with unusual equatorial placement of the coordinate Ge←O bond and the two carbons in axial positions in the trigonal bipyramidal environment for the metal, which are unusual for heavy group 14 elements[1a,2a] and make this path kinetically unfavorable. In contrast, the turnstile mechanism, having the only one-step exchange, is kinetically available. For this reason the pseudorotation is probably due to the turnstile mechanism as a most likely stage of the **B** → **B*** process for intramolecular ligand-site exchange (enantiomerization) in neutral hexacoordinated bischelate complexes **4**–**6**.

For complexes **4(a–c)**–**6** the remarkable changes in the activation barrier do not correlate with the d(Ge←O) bond distance, as is shown in Figure 4. This proved that there is no evidence that the rate of intramolecular exchange is controlled by dissociation of the Ge←O bond at the hexacoordinated center. However, there is the good linear correlation ($r = 0.996$) between the activation barrier for six-coordinated bischelates **4(a–c)** and **6** of the type $L_2Ge^{VI}Cl_2$ and the bond distance d(Ge←O) for pentacoordinated monochelates $LGe^{V}Me_2Cl$ with the same ligand L (Figure 4). This means that ligand exchange is readily controlled by the pseudorotation in the pentacoordinate species (process **B** ⇆ **B***, Figure 2). This result leads to the following two conclusions: (a) the dissociation–association process **A** ⇆ **B** (no exchange of the prochiral methylene protons occur) must be fast, and (b) the process **B** ⇆ **B*** is slow on the NMR time scale. Consequently, the pseudorotation for the pentacoordinate intermediate drives the enantiomerization process in hexacoordinate germanium bischelate complexes **4(a–c)**–**6**.

For germanium bischelates **4**–**6**, the observed free energies $\Delta G^{\ddagger} = 10.0$–$13.6$ kcal·mol^{-1} (Table 1) of enantiomerization for trigonal-bipyramidal intermediates are of the same order of magnitude as that observed for pseudorotation in pentacoordinated germanium complexes **19** with two bidentate chelate ligands, $\Delta G^{\ddagger} = 12.3$ (R = *t*-Bu) and 12.4 kcal·mol^{-1} (R = Ph),[62] and substantially lower than those of **20** with tridentate ligand, 19.1 (R = Me) and 21.3 kcal·mol^{-1} (R = Ph).[63]

For hexacoordinate germanium dichlorides **4**–**6** (L_2GeCl_2) the $\Delta G^{\ddagger}_{298}$ values (10.0–13.6 kcal·mol^{-1}, $CDCl_3$, Table 1) associated with the exchange process for the pentacoordinate dichlorides $LGeCl_2R$ (process **B** → **B***, Figure 2) are lower than in the known pentacoordinate monochlorides $LGeClMe_2$ with the same chelate ligand for pyrrolidone **21** (17.8 kcal·mol^{-1}) and acetamide **22a** (>23 kcal·mol^{-1}, Chart 5). This general tendency toward a decreasing $\Delta G^{\ddagger}$ value on increasing the number of halogens around the central atom is also observed for analogous (difluosilylmethyl)acetamide **23** ($\Delta G^{\ddagger} = 18.4$ kcal·mol^{-1}) compared with analogous (dimethylfluosilylmethyl)acetamide **22c** ($\Delta G^{\ddagger} > 24$ kcal·mol^{-1}) as well as for (difluosilylmethyl)- **24a** and (dichlosilylmethyl)-quinolinones **24b** as compared with the monohalides **24c** and **24d** (Chart 6).

The proposed mechanism of enantiomerization in dichlorides **4**–**6** and its consequences may be useful for a consistent analysis of the influence of the substituents X, coordinative bond lengths d(M←O), and nature of

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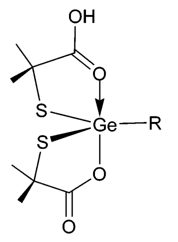
Chart 4



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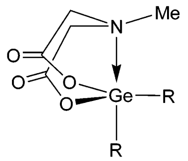

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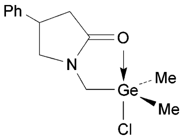
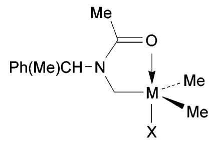
Chart 5



21 [52]

$\Delta G^{\neq}$ = 17.8 kcal·mol^{-1} ($CDCl_3$)
11.3 kcal·mol^{-1} (CD_3OD)
d(Ge←O) = 2.349 A



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	MX	$\Delta G^{\neq}$ (kcal·mol^{-1})			d(M←O) (Å)
		$CDCl_3$	CD_3CN	CD_3OD	
a	GeCl	>23 [52]	>20[52]	15.7[52]	2.203[52]
b	GeBr		17.0[52]	15.3[52,64]	2.138[52]
c	SiF	>24[29]	14.4[29]	12.0[29]	2.149[65]
d	SiCl	14.6 [66]	14.4 [66]	12.0[66]	1.975[65]
e	SiBr	14.9 [66]	14.2 [66]	11.9 [53,66]	
f	SnCl			12.5[64]	

central atom M on the stereodynamic behavior in analogous hexacoordinate compounds **1**–**3** and **7**–**12**. The known free energies of activation together with M←O bond distances for the germanium **1**–**8** and tin **9**–**12** bischelate complexes of the type L_2MX_2 (M = Ge and Sn; X = Hal) are summarized in Table 2. The calculated activation barriers $\Delta G^{\ddagger}_{298}$ are nearly the same as the $\Delta G^{\ddagger}(T_c)$ values obtained earlier at coalescence temperature.

The linear correlation between the $\Delta G^{\#}_{298}$ values for hexacoordinate dichlorides **4(a**–**c)** and **6** with the *d*(Ge←O) in known pentacoordinate dimethylgermanium chlorides has been revealed (Figure 4). It may be proposed that the same trend for the $\Delta G^{\#}_{298}$ is maintained with the Ge←O bond lengths in wide range of hexacoordinate germanium dihalides **1**–**8**, as they should correlate somehow with the pentacoordinate species. Thus, the shorter Ge←O distances, for example, in **1**, **4**, and **7** in the sequence **a** → **b** → **c** are regularly associated with the greater $\Delta G^{\ddagger}$ values (Table 2). As such, the significant shortening of the Ge←O bonds in these germanium dihalides for the same bidentate ligand in the order F > Cl > Br (Table 2) may suggest a simultaneously increasing of the barriers of enantiomerization also. However, the observed $\Delta G^{\#}$ values decrease, and a slight increase is observed only for complex **7c** (Table 2).

At the same time, the clearly pronounced tendency toward strengthening of the M←O coordination and simultaneously to decrease the barriers $\Delta G^{\#}$ as the halogen changes in the sequence F → Cl → Br is observed in the pentacoordinated monochelates **22** also. For example, for germanium acetamides **22a**,**b** the $\Delta G^{\#}$ value decreases by >4 kcal·mol^{-1} in CD_3CN (Chart 5) as the Cl atom ($d_{O\rightarrow Ge}$ = 2.203 Å, >20 kcal·mol^{-1}) is replaced by Br ($d_{O\rightarrow Ge}$ = 2.138 Å, 17.0 kcal·mol^{-1}). It is noteworthy that this effect in CD_3OD, possessing the higher solvating ability, is smaller, by 0.4 kcal·mol^{-1} (Chart 5). Similarly, the strengthening of the M←O bond and parallel weakening of the exchange barriers $\Delta G^{\ddagger}$ in $CDCl_3$ is observed for silicon complexes **22c**–**d**. Analogously, despite a lower electronegativity of the halogen X, shorter intermolecular dative M←O bonds are observed for pentacoordinate lactam **25**, ureas **26**, and quinolinone **27** complexes, as well as for silatranes **28** and germatranes **29** (Table 3).

Thus, the unusual sequence of barriers and the Ge←O bond lengths in hexacoordinate germanium **1**–**8** complexes resulting from the decreasing of the −I effect of the halogen X on going from F → Cl → Br is in the same order with the five-coordinate centers in **22** and **25**–**28**, which confirms the pentacoordinate intermediate is involved in the enantiomerization process of germanium dihalides **1**–**8**.

It should be noted that strengthening of the coordinate bond in the sequence F → Cl → Br (drastically different from increasing the electronegativity of the halogens) was supported for silicon adducts $H_3SiX{\cdot}NH_3$ (X = F, Cl, Br) by the ab initio calculations.[83] The same regularities were observed in bond lengths for the boron complexes of X_3B with NH_3[84] and adenine[85] also. Theoretical studies indicate that a stronger bonding in $Cl_3B{\leftarrow}NH_3$ compared with $F_3B{\leftarrow}NH_3$ adducts comes from the larger charge capacity of Lewis bases Cl_3B due to the larger and more polarizable halides that accommodate additional electron density more easily.[86]

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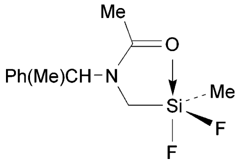
Chart 6



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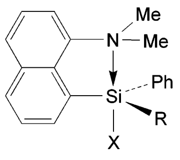
ΔG≠ = 18.4 kcal·mol^{-1} (CDCl$_3$)[67]



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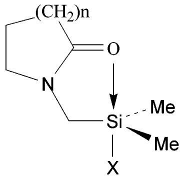
	X	R	ΔG≠ (kcal·mol^{-1})[68]
(**a**)	F	F	12
(**b**)	Cl	Cl	11
(**c**)	F	Me	23
(**d**)	Cl	Me	20
(**e**)	Br	Me	>20

Chart 7



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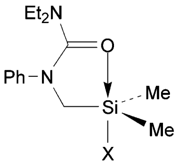

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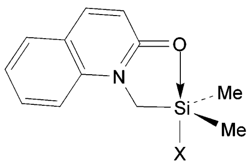

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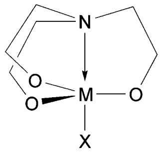

M = Si (**28**), Ge (**29**)

Although the barrier to the inversion of configuration in pentacoordinate germanium transition states for **1**–**8** decreasing in the series F → Cl → Br is opposite of the trend of the stronger Ge←O interaction, it is in order of greater halogen size. Hence, the pseudorotation process at the trigonal bipyramidal Ge center is a kinetic phenomenon, which depends on both ground state and transition state factors and is determined by the purely ground state properties such as not only the strengthening of the coordinate Ge←O bond due to chelate ligand constraints and the greater polarizability of the heavier halogens but also the steric interactions between substituents in the coordination sphere of the central atom. The unusual lowering of the barriers to pseudorotation for pentacoordinated germanium species is strongly affected on increasing the potential energy of the ground state, which may be caused by steric repulsions of bulkier halides.

As all complexes **1**–**11** of the type L$_2$MX$_2$ have similar *cis*-(M←O) structure (Table 2), the proposed mechanism of the enantiomerization may be readily transformed from germanium to tin derivatives. By analogy, the intramolecular ligand-exchange process (Figure 2) involving pseudorotation for the pentacoordinate transition state as the rate-limiting step can be expected for hexacoordinate tin complexes also. In this case they are likely to have a greater flexibility of the chelate ligands and a faster rate of enantiomerization, due to lengthening of the tin bonds (the covalent radius of the Sn atom is 1.48 Å[31] in comparison with 1.223 Å[31] for Ge). When all other factors remain the same, this is confirmed clearly by a strong decrease in the energy barrier $\Delta G^{\ddagger}$ in pentacoordinate chlorides **22** when replacing germanium (**22a**, 15.7 kcal·mol^{-1} in CD$_3$OD[64]) by tin (**22f**, 12.5 kcal·mol^{-1} [64,87]) (Chart 5). However, the observed $\Delta G^{\ddagger}$ values for tin dichlorides **9** and **10** (13.4–13.8 kcal·mol^{-1}) and dibromides **11** (13.5–13.8 kcal·mol^{-1}) are normally higher than those for germanium families **4** and **6** (10.0–12.3 kcal·mol^{-1}) and **7** (10.0–12.6 kcal·mol^{-1}) (Table 2). Therefore, it is possible to expect that a rate-limiting stage of the enantiomerization for hexacoordinate tin molecules **9**–**11** is not the result of pseudorotation in the trigonal bipyramidal intermediate state, but represents Sn←O bond rupture in the primary hexacoordinate state.

Although, for two hexacoordinated bischelate families the coordinate Ge←O bonds lengths in **1** and **4**–**7** are generally shorter than the Sn←O ones in **9**–**11** (Table 2), the larger covalent radius of the central Sn atom enhanced strengthening of the intramolecular M←O interaction. In contrast to germanium complexes, the slightly decreasing value of the energy barrier in the order X = Cl (13.6 kcal·mol^{-1}) > Br (13.5 kcal·mol^{-1}) > I (12.6 kcal·mol^{-1}) is observed only for tin derivatives **9a**, **11a**, and **12a** with five-membered lactam rings, i.e., for compounds with the weakest coordinate Sn←O bonds (Table 2). At the same time, an increase in the size of the lactam ring from five-membered (**a**) to seven-membered (**c**) in germanium complexes **4** and **7** and tin complexes **9** and **11** leads to a decrease in the *d*(M←O) distance by 0.086 (X = Cl)[26a] and 0.083 (X = Br)[27a] for Ge, which is significantly larger than 0.029 (X = Cl)[28b] and 0.025 (X = Br)[28c] for Sn. It is therefore evident that the smaller influence of halogen changes on the $\Delta G^{\#}$ values and smaller influence of chelate ligand structure on the coordination bonds are the result of the stronger intramolecular Sn←O interaction in hexacoordinate tin complexes **9**–**11** compared to germanium complexes **4**–**7**. Besides, the differences between the two *cis*-(M←O) bond lengths in the molecules of germanium dichlorides **4**(**a**–**c**),[26a] Δ*d*(Ge←O) = 0.056 Å (**a**), 0.127 Å (**b**), and 0.024 Å (**c**), are greater compared to Δ*d*(Sn←O) = 0.040 Å (**a**), 0.009 Å (**b**), and 0.023 Å (**c**) for tin dichlorides **9**(**a**–**c**),[28b] which can be ascribed to the smaller influence of the crystal packing effects[76b,88] on much stronger coordinate Sn←O bonds.

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Table 2. Comparison of the Barriers $\Delta G^{\#}$ and Entropy $\Delta S^{\ddagger}$ for Ligand Exchange (in $CDCl_3$) with Coordinate Bond Distances d(M←O) in Hexacoordinated (C,O)-Bischelate Complexes 1−12 of the Type *cis*-L_2MX_2 (M = Ge and Sn, X = Hal)[a]

$\Delta G^{\neq}_{298}$ and/or $\Delta G^{\neq}(T_c)^b$ (kcal·mol^{-1})						$\Delta S^{\neq}$ (cal·mol^{-1}·K^{-1})					d(M← O) average (Å)					
GeF_2[25]	$GeCl_2$[c]	$GeBr_2$	$SnCl_2$	$SnBr_2$	SnI_2[29]	GeF_2[25]	$GeCl_2$[c]	$GeBr_2$[69]	$SnCl_2$[69]	$SnBr_2$[69]	GeF_2[27a]	$GeCl_2$	$GeBr_2$[27a]	$SnCl_2$	$SnBr_2$[28c]	SnI_2[28c]
1a	**4a**	**7a**	**9a**	**11a**	**12a**	**1a**	**4a**	**7a**	**9a**	**11a**	**1a**	**4a**	**7a**	**9a**	**11a**	**12a**
12.1± 0.5	10.0	10.0± 0.2[69]	13.6± 0.3[69]	13.5± 0.2[69]		4.0± 1.9	7.3	3.9± 1.2	1.2± 1.1	1.5± 1.2	2.265	2.211[26a]	2.171	2.291[28b]	2.285	2.255
	10.6(225)[29]	10.2(218)[29]	13.6(270)[29]	13.3(279)[29]	12.6(274)											
1b	**4b**	**7b**	**9b**	**11b**	**12b**	**1b**	**4b**		**9b**	**11b**	**1b**	**4b**	**7b**	**9b**	**11b**	**12b**
13.9± 0.5	12.3		13.8± 0.3[69]	13.8± 0.3[69]		4.8± 1.9	15.3		3.7± 1.1	3.5± 1.1	2.209	2.146[26a]	2.100	2.260[28b]	2.261	2.270
	12.8(269)[29]	12.1(258)[29]	13.6(284)[29]	13.8(293)[29]	13.8(292)											
1c	**4c**	**7c**	**9c**	**11c**	**12c**	**1c**	**4c**	**7c**	**9c**	**11c**	**1c**	**4c**	**7c**	**9c**	**11c**	
13.6± 0.5	12.3	12.6± 0.4[69]	13.8± 0.3[69]	13.7± 0.3[69]		4.9± 1.9	15.3	5.5± 1.9	3.1± 1.2	4.1± 1.2	2.185	2.125[26a]	2.088	2.262[28b]	2.260	
	13.6(268)[29]	12.9(274)[29]	13.9(291)[29]	13.9(295)[29]	13.8(294)[29]											
2	**5**					**2**	**5**					**5**				
15.3 ±0 .5	13.6					5.1± 1.9	4.5					2.121[51]				
	13.7(290)[51]															
3	**6**	**8**	**10**			**3**	**6**	**8**	**10**			**6**		**10**		
13.5± 0.5	12.0	11.9± 0.3[69]	13.4± 0.2[69]			5.6± 1.9	10.0	8.2± 1.5	8.2± 1.0			2.110[26b]		2.257		
	12.1(256)[26b]	11.8(250)[27b]	13.0(279)[29]											2.259[d]		

[a] For the silicon analogue of difluoride **3** $\Delta G^{\ddagger}_{298}$ = 16.5 ± 0.3 kcal·mol^{-1}, $\Delta S^{\ddagger}$ = 8.5 ± 1.5 cal·mol^{-1}·K^{-1},[69] and d(M←O)$_{av}$ = 1.934 Å.[70] [b] The free activation energies obtained by the Eyring equation[47] at coalescence temperature T_c. [c] Our data of $\Delta G^{\ddagger}_{298}$ and $\Delta S^{\ddagger}$ (Table 1). [d] Two crystallographically independent molecules.[26b]

Table 3. Intramolecular Coordinate Bond Lengths in Pentacoordinated Monohalogeno Complexes 25−28

	25[71]		**26**[72]		**27**[73]	28	29
X		Si←O (Å)	(% Si−O)[a]	Si←O (Å)	Si←O	Si←N	Ge←N
F	N = 1	2.395_{av}[74]	(29)		2.065	2.042[75]	2.011[76] 2.104[77]
Cl	N = 2	1.954[78]	(55)	1.923	1.939	2.023[79]	2.096[77]
	N = 3	1.950[80]					
Br	N = 2	1.800[81]	(71)		1.852		2.090[82]

[a] Percentage Si−O bond formation was calculated using the ^{13}C chemical shifts of the aromatic ring carbons.

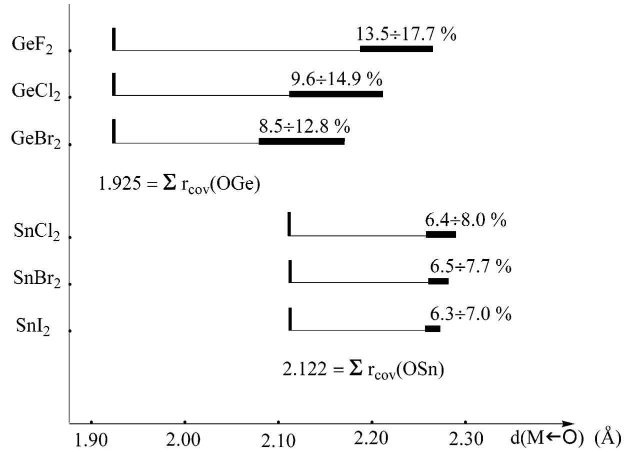

Figure 5. Ranges of differences between coordinate M←O bonds in germanium **1** and **4**−**7** and tin **9**−**12** dihalides (Table 2) and the sum of covalent radii for corresponding M and O atoms (in percent).

Since the energy of a dative bonding is less marked than that of covalent bonds, the difference between M←O bond lengths and the sum of covalent radii may serve as a criterion of relative bond strength, although it is known that the coordinate bond distances in donor−acceptor complexes often do not even qualitatively correlate with bond energies.[89] A comparison of the coordinate Sn←O and Ge←O bond lengths in two kinds of L_2MX_2 bischelates (Table 2) with the sum of the corresponding covalent radii visibly demonstrates stronger coordination in the tin complexes (Figure 5). For example, in dichlorostannanes **9**(**a**−**c**) and **10** the Sn←O distances (within the range 2.257−2.291 Å) exceed the sum of covalent radii by ca. 6.4−8.0%, which are smaller than ca. 9.6−14.9% for the corresponding dichlorogermanes **4**(**a**−**c**)−**6** (2.110−2.211 Å).

The increase in the barriers for ligand exchange on going from germanium **4**(**a**−**c**), **6**, and **7**(**a**−**c**) to the corresponding tin **9**(**a**−**c**), **10**, and **11**(**a**−**c**) families when all other factors remain the same is fully in accord with the strengthening of the intramolecular M←O coordination of the tin atom. This reflects a relatively

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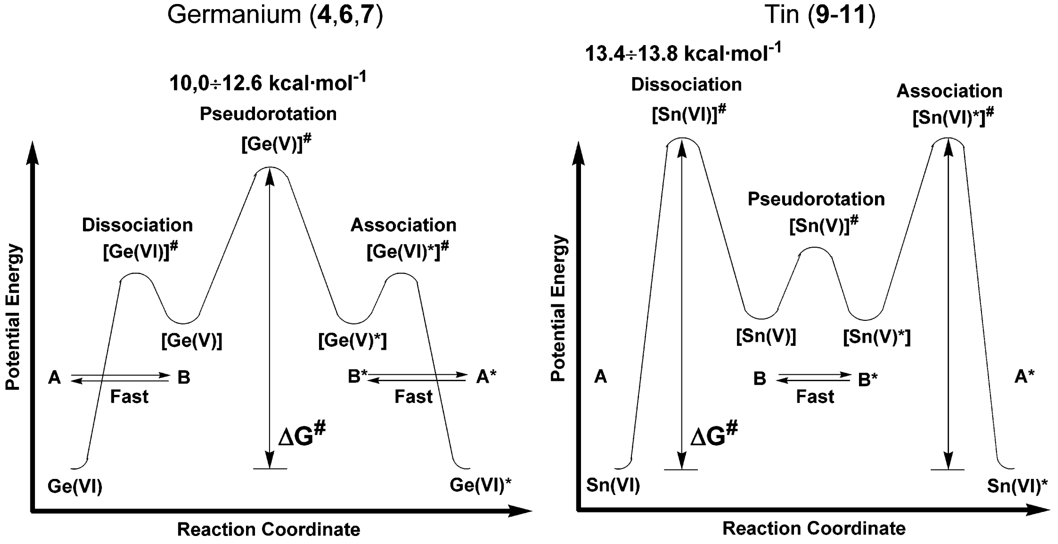


Figure 6. Free energy diagrams of the two-stage exchange process (Figure 2) for hexacoordinated complexes **1**−**12** of the type *cis*-L_2MX_2 (M =/Ge and Sn; X = Hal). For comparison, the $\Delta G^{\#}$ values for several germanium (**4**, **6**, and **7**) and tin (**9**−**11**) derivatives having identical chelate ligands L and substituents X are demonstrated. The free energy difference between two transition states for dissociation and pseudorotation leads to exchange of the rate-limiting step of enantiomerization for Ge and Sn atoms.

higher acceptor ability of the Sn atom, which is in accord with the general tendency toward strengthening of the M←O bond for higher row elements. Apparently, the same reason is responsible for the absence of consistent correlations between free energy of activation $\Delta G^{\ddagger}$ and the Sn←O distances in the hexacoordinated tin bischelates **9**−**11**.

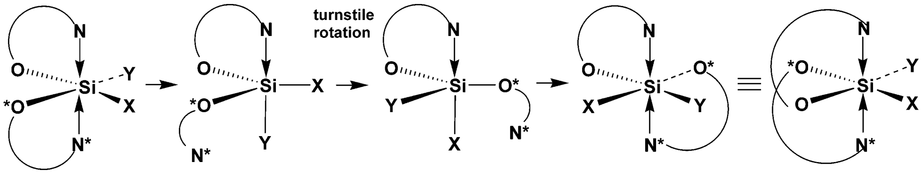
The distinctive features of enantiomerization for germanium **1**−**8** and tin **9**−**12** complexes discussed above can be interpreted in terms of the proposed dissociative mechanism (Scheme 2), in which only fast and slow processes may be changed; that is, for tin complexes **9**−**12** the first stage involving Sn←O bond rupture is the rate-limiting process. These can be referred to in connection with a model for the reaction coordinate for enantiomerization at germanium and tin complexes, as schematically shown in Figure 6.

A free energy versus reaction coordinate diagram for the enantiomerization indicates the $\Delta G^{\ddagger}$ for the rate-determining step. For germanium complexes **1**−**8**, the hexacoordinate transition state [Ge(VI)]$^{\#}$ is at lower energy relative to pentacoordinate [Ge(V)]$^{\#}$, and consequently the enantiomerization is determined by the pseudorotation (process **B** ⇆ **B***) in the trigonal bipyramidal intermediate [Ge(V)] that is formed fast. The replacement of the Ge atom at Sn leads to both strengthening of the M←O coordination and decreasing the exchange barrier for inversion at the trigonal bipyramidal transition state, and hence direct change of the rate-determining step for tin compounds. The activation free energy of the hexacoordinate transition state [Sn(VI)]$^{\#}$ is higher than pentacoordinate [Sn(V)]$^{\#}$, and hence the rate-limiting step of the enantiomerization is the Sn←O bond rupture (process **A** ⇆ **B**), while the pseudorotation for the intermediate [Sn(V)] is fast.

The positive entropy of the enantiomerization $\Delta S^{\#}$ (Table 2) in germanium **1**−**8** (4.5−15.3 cal·mol^{-1}·K^{-1}) and tin dihalides **9**−**11** (1.2−8.2 cal·mol^{-1}·K^{-1}) is most consistent with a mechanism where the transition state would either consist of pentacoordinated open-chain or be on its way toward open-chain, meaning greater disorder compared to the starting hexacoordinated cyclic structure. The distinct difference between entropies for germanium and tin complexes is due to a difference in the number of free internal rotations in five- and six-coordinated transition states. A rather higher entropy for germanium complexes **1**−**8** can be explanted with increasing the internal motion presumably due to an uncoordinated chelate ligand present in the pentacoordinated [Ge(V)]$^{\#}$ species. At the same time, the decreasing value of entropy in the analogous tin complexes **9**−**11** seems to indicate the decreasing in the internal degrees of freedom for the two bidentate chelate ligands because the formation of a fairly closed hexacoordinate transition state [Sn(VI)]$^{\#}$ takes place before Sn←O bond rupture.

On the assumption that the mechanism for Ge and Sn complexes is the same, it is possible to believe that the larger positive activation entropies for germanium complexes may be attributed to smaller degrees of freedom of the ligands in the ground state due to a shorter covalent bond length for the germanium atom. In this case the analogous silicon complexes may be also characterized by further increasing the positive entropies. In practice, however, for hexacoordinated *cis*-bis[(*N*-methylacetamido)methyl]difluorosilane (silicon analogue **3**) the positive entropy value $\Delta S^{\ddagger} = 8.5 \pm 1.5$ cal·mol^{-1}·K^{-1} (see footnote *a* in Table 2) is only slightly higher than 5.6 cal·mol^{-1}·K^{-1} found for complex **3** and is in the same range, 3.9−15.3 cal mol^{-1} K^{-1}, observed for other germanium complexes **1**−**8**. At the same time, in contrast to weaker coordination bonds for silicon atom, the silicon analogue **3** reveals increasing activation barrier, $\Delta G^{\ddagger}_{298} = 16.5 \pm 0.3$ kcal·mol^{-1},[69] as compared to 13.5 kcal·mol^{-1} for germanium difluoride **3** (Table 2). This is in accordance with the proposed dissociative mechanism (Figure 2); namely, the higher barrier of pseudorotation for the pentacoordinate silicon intermediate is accounted for by a shorter bond length for the silicon atom. Note that while the covalent radius of Ge is only slightly longer than that of the Si (by 0.05

Scheme 3. Irregular Process of the (L,L)-Exchange (Enantiomerization) in Hexacoordinate *trans*-(Si←N)-Complexes 14 Is Suggested on the Basis of Proposed Intramolecular Dissociative Mechanism (Figure 2)



Å), the corresponding difference between the Sn and Ge atoms is relatively larger (0.20 Å).[31]

The $\Delta S^{\ddagger}$ value for ligand-exchange process in **5** (4.5 cal·mol^{-1}·K^{-1}) is significantly smaller than in the other germanium dichlorides **4**(**a**−**c**) and **6**, resulting from the smaller flexibility of an uncoordinated chelate ligand in the pentacoordinate transition state [Ge(V)]$^{\#}$, which is most likely due to the increasing size of the benzooxazinone ligand and, consequently, to a larger steric interaction for the free rotation in the germanium coordination sphere. Perhaps for the same reason the barriers, $\Delta G^{\ddagger}_{298}$ = 13.6 kcal·mol^{-1}, for **5** are slightly higher than for the other germanium dichlorides coordinate bonds.

The proposed mechanism for (L,L)-exchange in dichlorogermanes **4**−**6** with *cis*-(Ge←O) structure (Figure 2) could successfully be used for the enantiomerization in hexacoordinated bischelates with *trans*-orientation of the two coordinate bonds, for example, in hexacoordinated silicon complexes **14** (Scheme 3). This conclusion is supported by the observation of a remarkable ^{29}Si chemical shift change in **14b**: an increase of temperature from 200 to 370 K (toluene-d_8) leads to low-field shifts of the ^{29}Si resonance from 263 to 118 ppm, indicating that the complex exists as an equilibrium of a hexacoordinate and a pentacoordinate species, with the latter as the predominant one at higher temperatures.[39k] This represents the clearly pronounced intramolecular exchange in solution between hexa- and pentacoordinate silicon complexes, indicating approximately the same thermodynamic stability of octahedral and trigonal-bipyramidal isomers.

In conclusion, the positive entropy of the enantiomerization in hexacoordinated bischelate complexes **1**−**12** of the type L_2MX_2 (M =/Ge and Sn; X = Hal) suggests that the inversion of configuration takes place through dissociative mechanisms. Two-step exchange processes are necessary to assist the overall pathway for the intramolecular isomerization. The different behavior between germanium and tin complexes observed for the ligand-site exchange is accounted for by the greater complexing ability and easier pseudorotational exchange for the Sn atom as compared to Ge. For germanium compounds **1**−**8** the rate of enantiomerization is controlled by the pseudorotation (**B** ⇆ **B*** process) in the pentacoordinate intermediate **B** (Figure 2). In contrast, the enantiomerization process for the tin analogues **9**−**12** is determined by the Sn←O bond rupture (**A** ⇆ **B** process) for the primary hexacoordinate species **A**.

Experimental Section

Complexes **4**−**6** were prepared from *N*-trimethylsilyl derivatives of corresponding lactams, 2,2-dimethylbenzo[2*H*]-4-oxazin-1,3-one-3-methyl or acetamide and bis(chloromethyl)-dichlorogermane (2:1), and fully characterized by ^{1}H and ^{13}C NMR.[26b,29,51,64,87] In this work the ^{1}H NMR spectra were recorded in $CDCl_3$, CD_3CN, acetone-d_6, and toluene-d_8 on a Bruker DRX500 spectrometer (500.130 MHz). A standard 5 mm ^{13}C−^{1}H probe head was used. The ^{1}H and ^{13}C chemical shifts were measured using Me_4Si as internal reference for ~0.2 M solutions. For processing of results standard mathematic programs of Bruker (XWINNMR 2.6 on Silicon Graphics Station with OS IRIX 6.4) were used. Temperature calibrations were performed using the distances between the nonequivalent protons of methanol (−90 to +30 °C).[90] Line shape analysis was performed using ^{1}H signals of the NCH_2Ge group. Activation parameters of the stereodynamic processes were calculated by means of DNMR-SIM[91] and DNMR5[92] software. Relaxation time was measured at each temperature point.

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