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Stereochemical non-rigidity of complexes of hypercoordinate Group 14 elements

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Abstract. Published data on stereodynamic processes in the coordination units of di- and tetravalent silicon, germanium, tin and lead compounds are summarized and analyzed. The bibliography includes 269 references.

I. Introduction

Compounds with non-classical types of chemical bond have become the subject of vigorous research in recent years.[1] These compounds include silicon,[2–10] germanium [11] and tin derivatives [11,12] in which the coordination sphere of the element is extended as a result of additional intra- or intermolecular coordination interaction.

The classical explanation for the ability of atoms of Group 14 tetravalent elements to increase the coordination number to five or six is based on participation of vacant d-orbitals in the formation of coordination bonds.[13–15] An alternative concept of increase in the coordination number is based on the view on three-centre four-electron (3c–4e) interactions.[16–26] Despite some criticism,[27,28] this model is used successfully to interpret the results of physicochemical studies. Compounds of this type can be used for modelling S_N2-substitution reactions at tetracoordinate atoms (see for example, papers [9,29–31]), which is important for investigation of the general trends of nucleophilic substitution involving organoelement compounds.

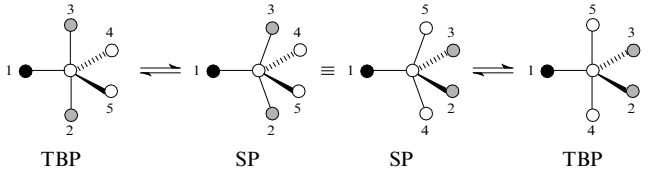
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Compounds of divalent Group 14 elements (heavy carbene analogues), unlike tetravalent ones, have a vacant *n*p-orbital of the central atom; hence, their molecules are expected to exhibit acceptor properties to a higher extent than tetravalent elements. As a rule, these compounds are susceptible for oligomerization and polymerization; therefore, the monomeric form can be stabilized either kinetically, by means of sterically crowded substituents, or thermodynamically owing to intramolecular coordination interactions. Many compounds of divalent Group 14 elements proved to be stable due to the stabilizing effect of bulky chelating ligands containing donor atoms (N, O, P and S).[32]

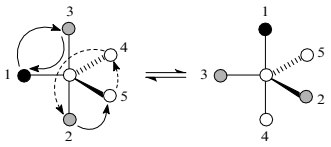
The stereochemical non-rigidity caused by relative ease of intra- (permutational isomerization) and/or intermolecular rearrangement of the coordination polyhedron is one of the most notable and perhaps least studied features of chelate complexes of di- and tetravalent Group 14 elements. The mechanisms of stereodynamic processes in the coordination unit of these complexes can be conventionally divided into non-dissociative and dissociative ones.

For pentacoordinate complexes, non-dissociative (regular) mechanisms include reversible transition between trigonal-bipyramidal (TBP) configurations through a square pyramid (SP) (Berry pseudorotation).[33–35] After completion of the cycle, the molecule with five identical ligands acquires a shape identical to the initial one. The relative ease of interconversion between forms is due to similarity of TBP and SP energies.



An alternative to this interconversion is the turnstile rotation [36,37] characterized by higher activation energies

($\Delta G^{\#} > 12$ kcal mol^{-1}) than the Berry pseudorotation (2–8 kcal mol^{-1}).[33–35]



According to non-dissociative mechanism, the permutation processes in hexacoordinate complexes are described as trigonal[38] and digonal[39,40] twists (Bailar twist and Rey–Dutt twist, respectively). Their topology was described in detail.[41]

The dissociative (irregular) mechanisms in hypercoordinate element complexes are accomplished through bond cleavage and subsequent recovery.[42,43]

The predominant mechanism of permutational isomerization in the coordination unit of Group 14 element complexes is largely determined by the nature of bonds at the central atom, which can be investigated by quantum chemistry methods. A large number of studies in this field have now been reported.[44–54] Unfortunately, due to a number of limitations, detailed discussion of this issue could not be included in this review.

As a rule, the rate of stereodynamic processes in the molecules varies from 10^{-1} to 10^{5} s^{-1}, and NMR spectroscopy is the only method suitable for their investigation. This fact accelerated the development of dynamic NMR (DNMR) theory and promoted its practical application, in particular, in organoelement chemistry. Since first fundamental works in this field,[55,56] a number of monographs and comprehensive reviews devoted to theoretical and applied aspects of the DNMR method appeared.[57–68]

Two procedural approaches to determination of the activation parameters of stereodynamic processes are known. The first one includes the calculation of the activation free energy for the exchange ($\Delta G^{\#}$) at signal coalescence temperature (T_c) using the modified Eyring equation:[60]

$$\Delta G^{\#} = (4.57 \times 10^{-3}) T_c \left[10.32 + \log \left(\frac{T_c \sqrt{2}}{\pi \Delta \nu} \right) \right], \qquad (1)$$

where T_c is the coalescence temperature (in Kelvins), $\Delta\nu$ is the difference between the resonance frequencies of the exchanging nuclei (in Hertz).

If the activation free energy for the exchange at the coalescence point is calculated for a series of compounds with similar structure, the systematic errors can be neglected and the $\Delta G^{\#}$ values can be determined with high accuracy. Indeed, in precision experiments where the temperature is determined to an accuracy of ± 0.5 deg, the error in determination of $\Delta G^{\#}$ can be up to ± 1 kcal mol^{-1}. Important limitations of this approach are the facts that it does not provide quantitative data on the activation enthalpy and entropy and certain difficulties of comparison of $\Delta G^{\#}$ values calculated at different coalescence temperatures.

The other approach devoid of this drawback is based on full line shape analysis of NMR signals from the exchanging nuclei. For a sufficient number of experimental points, the least-squares method, despite its certain limitations,[65] gives a random error in $\Delta H^{\#}$ and ΔS estimation comparable with the limiting accuracy in a precision experiment. However, the least-squares method does not take into account the errors in temperature measurement and, what is more important, the rate constants, which increase considerably for statistically significant temperatures far from the coalescence point.[58]

II. Neutral pentacoordinate complexes of tetravalent elements

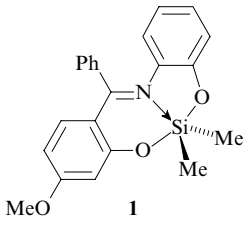
Intramolecular ligand exchange in pentacoordinate Group 14 element complexes is slower due to the chelation effect. This fact allows using multinuclear DNMR for investigation of stereodynamic processes.

1. Complexes with N → Si coordination bond

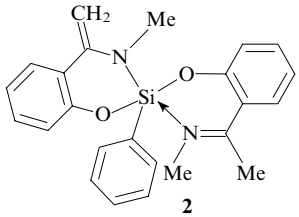
Most intramolecular complexes of pentacoordinate silicon contain a five-membered chelate ring. The length of the intramolecular coordination bond N → Si varies in the range of 1.8 to 2.6 Å depending on the structure, type and the number of electronegative ligands.[9] The thermodynamic parameters of N → Si bond dissociation for compounds **1**, **2** are as follows:

Complex	ΔH_d /kcal mol^{-1}	ΔS_d /cal mol^{-1} K^{-1}	Ref.
1	1.52	5.12	69
2	7.53	−27.91	70

According to quantum chemical calculations [MP2/6-311 + G(2d,p)], the formation of a TBP structure for complex **2** is exothermic ($\Delta H = -6$ kcal mol^{-1}).[70] Low dissociation energies of the N → Si intramolecular coordination bond (< 9 kcal mol^{-1}) were also calculated [DFT, M2P/6-31G(d)] for the series of complexes $H_3N \rightarrow Si(OH)_n Me_{4-n}$ ($n = 1-3$).[71]



1



2

Stabilization of intramolecular coordination bond is promoted by the presence of an electronegative ligand. In the complexes Z → $SiXR_3$ (Z = N, O; X is an electronegative ligand), Z and X occupy axial positions thus forming a linear fragment Z → Si–X. As the number of electronegative ligands increases, the probability of elimination of the axial group X decreases in the series Cl, OC(O)R > F ≈ SR > OR, NR_2 > Ar > Alk > H.[72]

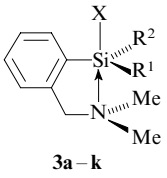
a. Complexes with one monodentate electronegative substituent

In complexes **3** and **4**, an increase in the nucleofugacity of monodentate electronegative ligand X in the series SEt < F < OAc < Cl < Br is accompanied by parallel variation of $\Delta G^{\#}$ (Table 1).[73–76] In the authors' opinion, this attests to irregular (dissociation of the monodentate ligand) mechanism of permutational isomerization, resulting in exchange of positions of monodentate equatorial ligands.[73–76]

Table 1. Activation barriers to permutation and coalescence temperatures of NMR signals for complexes **3**–**7**.[73–83]

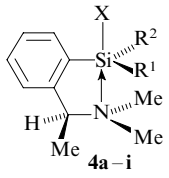
Complex	Solvent	$\Delta G^{\#}$ /kcal mol^{-1}	T_c/°C	Complex	Solvent	$\Delta G^{\#}$ /kcal mol^{-1}	T_c/°C
3a	CD_2Cl_2	10.8	−65	**4i**	CD_2Cl_2	16.7	60
3b	CD_2Cl_2	11.5	−52	**5a**	CD_2Cl_2	< 7.0	< −100
3c	CD_2Cl_2	11.7	−46	**5b**	*o*-$Cl_2C_6D_4$	22.0	160
3d	CD_2Cl_2	12.3	−40	**5c**	*o*-$Cl_2C_6D_4$	20.0	130
3e	CD_2Cl_2	13.8	−10	**5d**	*o*-$Cl_2C_6D_4$	> 19.0	> 110
3f	CD_2Cl_2	10.3	−65	**5e**	*o*-$Cl_2C_6D_4$	22.0	175
3g	CD_2Cl_2	12.0	−35	**5f**	*o*-$Cl_2C_6D_4$	23.0	200
	CCl_4	13.0	1	**5g**	*o*-$Cl_2C_6D_4$	> 22.0	> 160
3h	CD_2Cl_2	12.3	−35	**5h**	*o*-$Cl_2C_6D_4$	22.0	160
	$CDCl_3$	13.0	16	**5i**	*o*-$Cl_2C_6D_4$	21.0	200
	$CCl_4 + CD_2Cl_2$	11.8	−40	**6a**	CD_2Cl_2	10.2[b]	—
3i	$CCl_4 + CDCl_3$	13.0	1	**6b**	CD_2Cl_2	10.5[c]	—
3j	$CCl_4 + CD_2Cl_2$	13.0	16	**7a**	$CDCl_3$	14.6	—
3k	$CCl_4 + CD_2Cl_2$	13.8	−10	**7c**	CD_2Cl_2	10.9	—
4a	$CCl_4 + CDCl_3$	9.7	−70	**7d**	CD_2Cl_2	11.0	—
4b	$CCl_4 + CD_2Cl_2$	10.0	−73	**7e**	CD_2Cl_2	11.4	—
4c	$CCl_4 + CDCl_3$	13.4, 14.3[a]	10	**7f**	CD_2Cl_2	10.6	—
4d	$CCl_4 + CD_2Cl_2$	13.6, 14.1[a]	12	**7g**	CD_2Cl_2	10.7	—
4e	CD_2Cl_2	10.0	−66	**7h**	CD_2Cl_2	9.4	—
4f	CD_2Cl_2	9.0	−86	**7i**	CD_2Cl_2	8.9	—
4g	CD_2Cl_2	9.7	−72	**7j**	CD_2Cl_2	< 7.0	—
4h	CD_2Cl_2	10.0	−65				

[a] The spectrum exhibits signals for two diastereomers. [b] The $\Delta G^{\#}$ values calculated at the coalescence temperature of the SiH_2-, NMe_2-, NCH_2-group protons are equal. [c] The $\Delta G^{\#}$ values calculated at the coalescence temperature of NMe_2- and NCH_2-group protons are 10.8 and 10.5 kcal mol^{-1}, respectively.



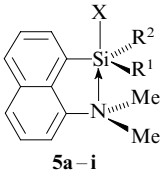
3a–**k**

R^2 = Me, R^1 = H: X = SEt (**a**), F (**b**), OAc (**c**), Cl (**d**), Br (**e**); R^1 = 1-Naph: X = F (**f**), OAc (**g**), Cl (**h**); R^1 = 1-Naph, R^2 = H: X = Cl (**i**), OAc (**j**), Br (**k**); 1-Naph is 1-naphthyl .



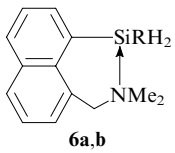
4a–**i**

X = F, R^1 = Me: R^2 = Me (**a**), Ph (**b**); X = Cl, R^2 = H: R^1 = Ph (**c**), 1-Naph (**d**); X = R^2 = H: R^1 = H (**e**), Me (**f**), 1-Naph (**g**), Ph (**h**); R^1 = R^2 = H, X = Cl (**i**).



5a–**i**

R^1 = R^2 = X = H (**a**), R^1 = Ph, R^2 = Me: X = H (**b**), F (**c**), Cl (**d**), Br (**e**), OMe (**f**); R^1 = H, X = Cl: R^2 = Ph (**g**), Me (**h**); R^1 = H, R^2 = Ph, X = Br (**i**).

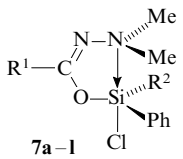


6a,**b**

R = H (**a**), Ph (**b**).

The increase in $\Delta G^{\#}$ by more than 10 kcal mol^{-1} with an increase in the size of the bidentate ligand on passing from *ortho*-substituted benzene derivatives (complexes **3** and **4**) to 1,8-substituted naphthalene derivatives (compounds **5b**–**i**) may be due to greater steric effect of two fused benzene rings for the transition state. In this case, unlike complexes **3** and **4**, variation of nucleofugacity of the monodentate ligand X (F, Cl, Br, OMe, Ph) has no noticeable influence on $\Delta G^{\#}$ ($\sim$20–22 kcal mol^{-1}). However, in the case of six-membered chelate ring (complex **6b**), the barrier to permutational isomerization (10.5 kcal mol^{-1}) is much lower than that for analogous complex **5b** with more stable five-membered chelate ring (22 kcal mol^{-1}, see Table 1). An exception is complex **5a** with the SiH_3 coordination unit in which steric interactions are insignificant ($\Delta G^{\#}$ < 7 kcal mol^{-1}).

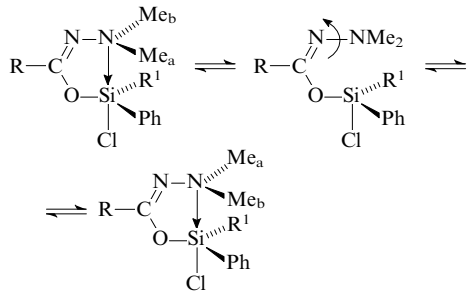
The increase in the nucleofugacity of the substituent R^1 in the chelating ligand of complexes **7a**–**l** resulting in a decrease in the intramolecular coordination bond length is accompanied by a decrease in the barrier to permutation (see Table 1).[77–83]



7a–**l**

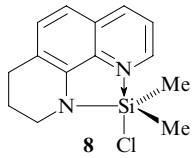
R^2 = H: R^1 = Ph (**a**), CH(Me)Ph (**b**); R^2 = Me: R^1 = Me (**c**), CH_2Ph (**d**), CH(Me)Ph (**e**), Ph (**f**), 4-MeC_6H_4 (**g**), 4-$NO_2C_6H_4$ (**h**), 3,5-$(NO_2)_2C_6H_3$ (**i**), CF_3 (**j**); R^1 = CH(Me)Ph: R^2 = H (**k**), Me (**l**).

As a result, an intramolecular mechanism of permutation through reversible dissociation of the N → Si bond with subsequent nitrogen inversion was proposed.



The ^1H and ^{13}C NMR spectra of complexes **7b**,**e** with two chiral centers (silicon and carbon atoms) under slow exchange conditions (-50 °C, in $CDCl_3$) contain signals for two diastereomers.[77,82] The interconversion barrier for the diastereomers of complex **7e** is much higher (> 18.7 kcal mol^{-1}) than the value ~11.4 kcal mol^{-1} calculated for the exchange of NMe_2 groups (see Table 1).

In the opinion of the authors,[84,85] the permutation barrier for complex **8** (~18 kcal mol^{-1} in CD_2Cl_2) corresponds to the dissociative mechanism with N → Si bond cleavage.



8

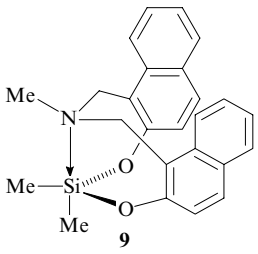
Note, however, that this high $\Delta G^{\#}$ value for a relatively polar solvent casts doubt upon this conclusion. An alternative is elimination of Cl^- in polar solvents to give a tetracoordinate ionic intermediate or transition state followed by inversion of Si configuration as a result of frontal attack of Cl^- or the formation of topomers with diequatorial bidentate ligand during the Berry pseudorotation. Note that high $\Delta G^{\#}$ values can also be caused by steric hindrance for the turnstile rotation.

Table 2 summarizes the $\Delta G^{\#}$ values for permutational isomerization in complexes **9**–**11** resulting in averaging of signals from Me groups and benzene *ortho*-protons. The barriers were calculated from DNMR data using Eqn (1).[86–89]

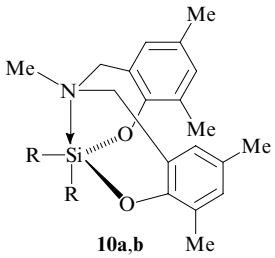
Table 2. Activation barriers to permutation and coalescence temperatures of NMR signals for complexes **9**–**11**.[86–89]

Complex	Solvent	Group	$\Delta\nu$/Hz	T_c/°C	$\Delta G^{\#}$ (see [a])	$\Delta G^{\#}_{av}$ (see [b])
9	CD_2Cl_2	NCH_2	36.0	−83	9.3	9.2
		SiMe	194.54	−73	9.1	
10a	$CDCl_3$	NCH_2	200.68	−50	10.2	10.2
		SiMe	156.28	−53	10.2	
	$C_6D_5CD_3$	NCH_2	296.32	−48	10.2	10.2
		SiMe	212.94	−51	10.2	
10b	$C_6D_5CD_3$	NCH_2	68.94	−55	10.5	10.4
		SiPh [c]	63.88	−57	10.4	
11a	$C_6D_5CD_3$	–	–	–	–	10.7
11b	$C_6D_5CD_3$	–	–	–	–	13.0
11c	$C_6D_5CD_3$	–	–	–	–	13.2
11d	$C_6D_5CD_3$	–	–	–	–	13.5

[a] In kcal mol^{-1}. [b] Averaged parameter, in kcal mol^{-1}. [c] Calculated based on the signal of the *ortho*-proton.

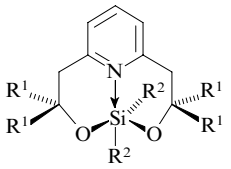


9



10a,**b**

R = Me (**a**), Ph (**b**).



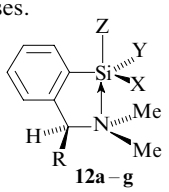
11a–**d**

R^1 = 4-FC_6H_4: R^2 = Me (**a**), Ph (**b**);
R^1 = R^2 = Ph (**c**);
R^1–R^1 is adamantylidene,
R^2 = Ph (**d**).

As can be seen from the presented data, the replacement of Me by Ph and a change in the solvent polarity do not affect the activation barrier to permutation in complexes **9**–**11**. Meanwhile, an increase in the size of substituents R^1 and R^2 on going to complexes **11** is accompanied by a considerable increase in $\Delta G^{\#}$ (see Table 2).

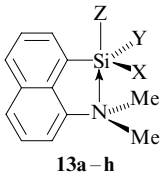
b. Complexes with several monodentate electronegative substituents

The much lower barrier to permutation for silicon chelate complexes **12** and **13** with two or three electronegative ligands (7–9 kcal mol^{-1})[85,89] compared to complexes with one ligand (> 14 kcal mol^{-1}) (Tables 1 and 3) attests to different mechanisms of stereodynamic process in these two cases.



12a–**g**

R = H: X = Me, Y = OMe, Z = F (**a**);
X = 1-Naph, Y = Z = Cl (**b**);
X = Me, Y = F, Z = Cl (**c**);
X = Y = Z = F (**d**); R = Me: X = Ph,
Y = Z = OMe (**e**); X = Me, Y = Z = F (**f**);
X = Ph, Y = Z = Cl (**g**).



13a–**h**

X = Ph: Y = Z = Cl (**a**), F (**b**), OMe (**c**);
Y = Z = Cl: X = Me (**d**), H (**e**);
X = Y = Z = F (**f**), OMe (**g**), OEt (**h**).

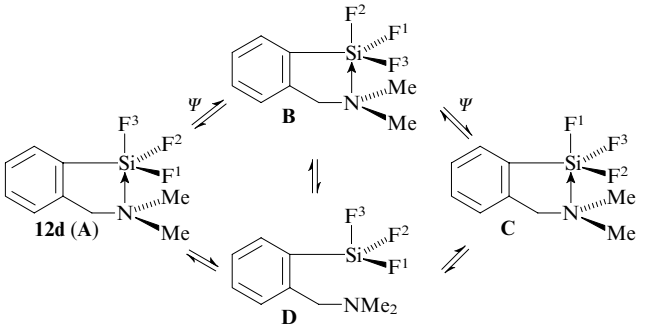
Table 3. Activation barriers to permutation and coalescence temperatures of NMR signals for complexes **12** and **13** in CD_2Cl_2.[85,89]

Complex	$\Delta G^{\#}$ /kcal mol^{-1}	T_c/°C	Complex	$\Delta G^{\#}$, /kcal mol^{-1}	T_c/°C
12a	9.0	−90	**12h**	7.6	−110
12b (see [a])	10.6	−50	**13a**	11.0	−43
12c (see [a])	11.8	−40	**13b**	12.0	−26
12d	11.7	0	**13c**	9.0	−84
12e	< 8.0	< −110	**13d**	9.0	−75
12f	9.4,[b] 11.8 [c]	−75,[b]	**13e**	10.2	−62
		−25 [c]	**13f**	12.0	20
12g	11.1,[b] 12.2 [c]	−45,[b]	**13g**	< 7.0	< −100
		−17 [c]	**13h**	< 7.0	–

[a] In the case of complexes **12b** and **12c**, mixtures $CCl_4 + CDCl_3$ and $CCl_4 + CD_2Cl_2$, respectively, were used as solvents. [b] Determined with respect to the chiral silicon atom. [c] Determined with respect to the chiral carbon atom.

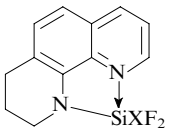
In complexes **12d**,**f**,**g** two stereodynamic processes were found: a low-temperature process corresponding to pseudorotation and a high-temperature process attributed to dissociation of the N → Si bond.[72] The retention of the spin-spin coupling constant $^1J_{Si-F}$ over a broad temperature range (from −100 to +60 °C) attests, in the authors' opinion, to the absence of intermolecular exchange involving fluorine atoms.

The turnstile rotation (**A** ⇄ **B** ⇄ **C**), an equilibrium involving the open and ring forms (**A** ⇄ **D** ⇄ **C**) and a combination of these processes have been considered as possible mechanisms of permutation in the coordination unit of trifluorides **12d** and **13f**.[72]



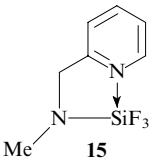
The decrease in the N → Si bond length on going from mono- to di- and then to trifluorides would have increased the barrier to permutation along the route **A** ⇄ **D** ⇄ **C**, which is at variance with published data.[72,73] Therefore, in our opinion, permutation by the regular mechanism **A** ⇄ **B** ⇄ **C** is more likely.

It was suggested[84,85] that the ligand permutation in complexes **14a**,**b** follows an intramolecular irregular mechanism with N → Si bond cleavage. The barriers to permutation determined by DNMR (in CD_2Cl_2) were 10.1 and 9.9 kcal mol^{-1}, respectively. These values exceed insignificantly the values calculated by MNDO for complexes **14a** and **15** ($\Delta G^{\#}$ = 7.5 and 7.7 kcal mol^{-1}, respectively).[84,85]

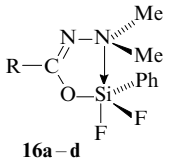


14a,**b**

X = F (**a**), Cl (**b**).

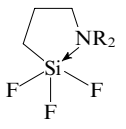


15



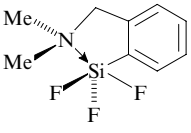
16a–**d**

R = Me (**a**), Ph (**b**), CH_2Ph (**c**), CH(Me)Ph (**d**).



17a,**b**

R = H (**a**), Me (**b**).



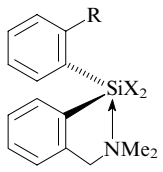
18

In difluorides **16**, permutation is fast on the NMR time scale: even at temperatures below −90 °C, the fluorine signals in the ^{19}F NMR spectra remain equivalent. Therefore, the activation parameters of the process cannot be calculated.[83]

The activation barriers to permutation in trifluorides **17a**,**b** determined by ^{19}F DNMR were 9.2 and 8.8 kcal mol^{-1}, respectively.[90] Upon comparison of the ^{29}Si NMR spectral parameters and $\Delta G^{\#}$ values for complexes **17a**,**b** and **18** (9.9 kcal mol^{-1}),[91] it was concluded that a stronger intramolecular coordination bond is formed in the latter case.

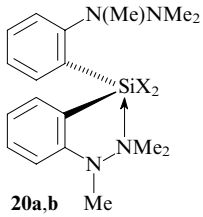
In the ^{1}H NMR spectra of complexes **19** and **20**, the signals of non-equivalent protons of the CH_2 and NMe groups are recorded as singlets, which is indicative of silicon pentacoordination.[92,93] As the temperature decreases, the signals are broadened (equimolar mixture of $CDCl_3$ and CD_2Cl_2), and finally two signlets for each of the indicator groups are observed at −90 °C. The following activation barriers were calculated:

Complex	ΔG /kcal mol^{-1}	Ref.
19a	9.7	92
19b	11.1	92
20a	9.8	93
20b	11.5	93



19a–**c**

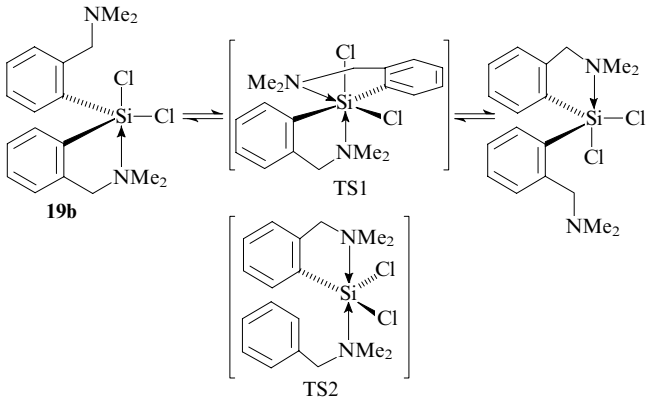
X = Cl: R = H (**a**), CH_2NMe_2 (**b**); X = OEt, R = CH_2NMe_2 (**c**).



20a,**b**

X = OEt (**a**), Cl (**b**).

For stereodynamic transformations in complexes **19b**, **20a**,**b** with two electron-donating centres (nitrogen atoms), a mechanism involving intermediate hexacoordinate transition state has been proposed.[92,93] According to ^{1}H NMR spectroscopy, transition state has C_2 symmetry, *trans*-arrangement of N and Cl being preferred from the energy standpoint (*i.e.*, TS1 rather than TS2).



19b

TS1

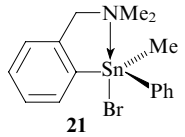
TS2

The ^{1}H NMR spectrum of complex **19c** at −93 °C is identical to the spectrum at room temperature, which was attributed to a fast, on the NMR time scale, exchange between two isomers.[94] A similar process was found for 2,4,6-tris[(dimethylamino)methyl]phenoxysilanes.[95]

2. Complexes with N → Sn coordination bond

The equivalence of NMe_2-group protons observed in the ^{1}H NMR spectra of bromide **21** at room temperature may be caused by two processes: (1) configuration inversion of the tin atom in the pentacoordinate conformer and (2) dissociation of the N → Sn bond followed by inversion of

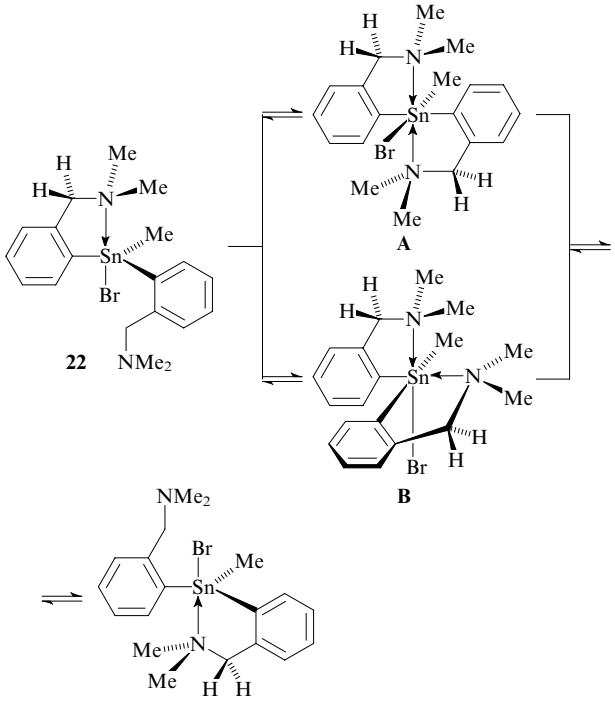
nitrogen, rotation through 180° around the CH_2-N bond and formation of a new $N \rightarrow Sn$ bond.[96]



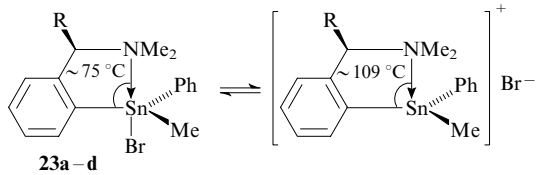
21

The $\Delta G^{\#}$ value (> 20 kcal mol^{-1}) exceeds considerably the activation energy for the pyramidal inversion of nitrogen in *N*,*N*-dialkylbenzylamines (< 6 kcal mol^{-1}).[61] Therefore, the latter process was preferred.[96]

Unlike bromide **21** with one electron-donating nitrogen atom, the mechanism of ligand permutation in bis-chelate complex **22** includes, in the authors' opinion, the formation of hexacoordinate intermediates with *trans*- (**A**) or *cis*-arrangement (**B**) of the intramolecular coordination bond.[97]

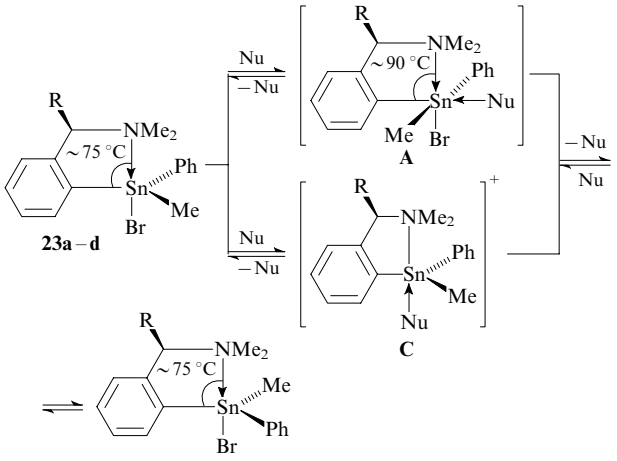


The position exchange of the equatorial ligands Ph and Me in the complexes **23a**–**d** with two chiral centres (carbon and tin atoms) occurs apparently without cleavage of the intramolecular coordination bond.[98]



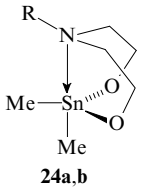
R = Me (**a**), Et (**b**), Pr^{i} (**c**), Bu^{t} (**d**).

The probability of dissociative mechanism with elimination of Br^- anion requiring considerable change in the chelate ring geometry is relatively low compared with the associative mechanism involving nucleophile (Nu). In the latter case, stereoisomerization occurs either through hexacoordinate intermediate **A** or through sterically more strained pentacoordinate cation **C**.[98]

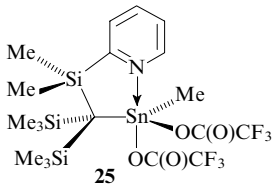


In the ^{1}H NMR spectrum of the complex [2-(Me_2NCH_2)C_6H_4]$SnCl_3$ in $CDCl_3$, the CH_2 and NMe_2 proton signals appear as a somewhat broadened singlet even at −60 °C, which is indicative of fast, on the NMR time scale, position exchange in the coordination unit involving three chlorine atoms.[99] Similar fast processes are typical of silicon complexes with several electron-withdrawing substituents (Section II.1.b).

The calculated barriers to permutation for complexes **24a**,**b** are higher (Table 4) than those for silicon analogues **10** and **11** (see Table 2).[100] Experimental data do not contradict the dissociative permutation mechanism with $N \rightarrow Sn$ bond cleavage and subsequent inversion of nitrogen.[100]



24a,**b**



25

R = H (**a**), Me (**b**).

Table 4. Activation parameters of permutational isomerization for complexes **24**.[100]

Complex	Solvent	$\Delta G^{\#}$1 (see [a])	T_c/°C	$\Delta H^{\#}$ (see [a])	E_a (see [a])
24a	$CDCl_3$	15 ± 1	11	12 ± 3	12 ± 3
	$(CD_3)_2CO$	16 ± 1	24	23 ± 3	23 ± 3
24b	$CDCl_3$	15 ± 1	10	21 ± 3	21 ± 3
	$(CD_3)_2CO$	15 ± 1	13	22 ± 3	22 ± 3

[a] In kcal mol^{-1}.

Dissociative mechanism (reversible cleavage of intramolecular coordination bond) was proposed to interpret the exchange of $OC(O)CF_3$ groups ($\Delta G^{\#}$ = 14.8 kcal mol^{-1}) observed in the ^{1}H and ^{19}F NMR spectra (in THF) of complex **25**.[101]

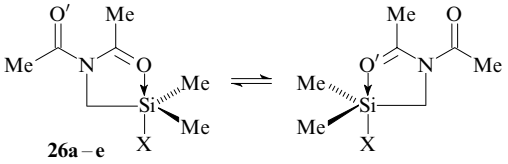
The ^{13}C NMR spectrum of complex $(Me_2NCH_2.CH_2O)_2SnFe(CO)_4$ recorded at room temperature exhibits only one signal corresponding to two carbonyl carbon atoms.[102] In the authors' opinion, this attests to a fast (on the NMR time scale) stereodynamic process involving bidentate ligands. According to DFT quantum chemical calculations, the activation barrier for this process was estimated [102] as 1.6 kcal mol^{-1}.

3. Complexes with O → Si coordination bond

a. Complexes with one electronegative substituent

Most neutral monochelate complexes with O → Si bond contain a five-membered chelate ring and have a nearly TBP geometry.[103, 104] The average length of the O → Si bond determined over 481 compounds was 1.699 Å.[105]

Migration of O → Si bond between two donor centres was first described in a number of studies [81, 106, 107] in relation to degenerate isomerization of Si-substituted (O−Si)-dimethyl(*N*-acetylacetaminomethyl)silanes **26**.



26a–e

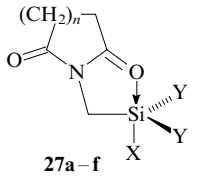
X = Cl (**a**), Br (**b**), I (**c**), OAc (**d**), $OC(O)CF_3$ (**e**).

The migration of intramolecular coordination bond between the oxygen atoms of two acetyl groups includes its dissociation, rotation around the C−N bonds and formation of a new O → Si bond with the oxygen atom of the other acetyl group. The activation free energy for the degenerate isomerization (7.7–10.5 kcal mol^{-1}, Table 5) is close to typical barriers to hindered rotation around the amide bond in *N*-diacetyl derivatives of aliphatic amines.[108] The $\Delta G^{\#}$ value increases upon variation of X in the series OAc ≪ Cl < $OC(O)CF_3$, Br ≪ I, which corresponds to strengthening of the O → Si bond (decrease in its length). This prompted authors [106] to suggest that the energy expenditure for dissociation of intramolecular coordination bond dissociation determines the process thermodynamics and the capability of this bond for migration.

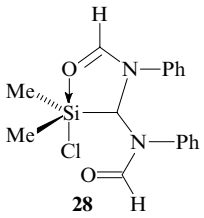
Table 5. Activation free energy of migration of the O → Si ICB and coalescence temperatures of indicator signals in the ^1H and ^{13}C NMR spectra of compounds **26a–e**.[106]

Compound	T_c/°C		$\Delta G^{\#}$/kcal mol^{-1}	
	CH_3	C=O	CH_3	C=O
26a	−100	−88	8.3	8.5
26b	−82	−70	9.3	9.3
26c	−55	−45	10.6	10.4
26d	−108	−101	7.8	7.7
26e	−90	−70	9.2	9.5

The competitive n,π-conjugation of the lone electron pair of nitrogen with two C=O carbonyl groups in five- (**27a**,**b**) and six-membered (**27c**,**d**) imides is less efficient than in the above-considered amides with one C=O group. This results in a decrease in the electron-donating ability of oxygen atoms and explains the degenerate isomerization in complexes **27** and **28** fast on the NMR time scale.[109–117]



27a–f

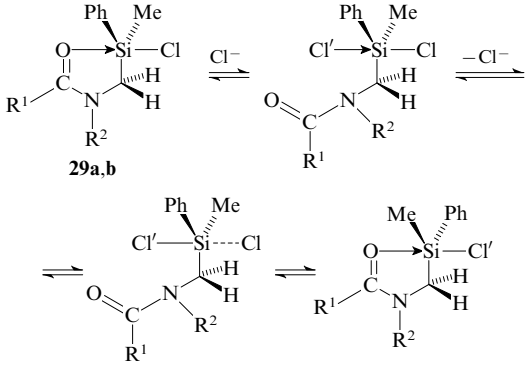


28

n = 1, Y = Me: X = F (**a**), Cl (**b**);
n = 2, Y = Me: X = F (**c**), Cl (**d**);
X = Y = F: n = 1 (**e**), n = 2 (**f**).

For complex **27e**, the free energy of 'transcoordination' was determined by ^{19}F DNMR (8.5 kcal mol^{-1}); taking into account the error of measurement, this is close to the value 8.4 kcal mol^{-1} found by ^{13}C DNMR.[113]

The dynamic process resulting in averaging of NCH_2 proton signals at elevated temperature in $CDCl_3$ also takes place in complexes **29** with different monodentate equatorial ligands.[118] The dissociative-associative mechanism includes Si−O bond cleavage, attack of the chloride anion on silicon with inversion of silicon configuration and then restoration of the oxygen coordination to silicon.



29a,**b**

$R^1 = NEt_2$, R^2 = Ph (**a**); $R^1 = R^2$ = Me (**b**).

The dependences of the activation parameters of permutational isomerization in Si-substituted *N*-(silylmethyl)-amides, lactams and related compounds (complexes **30–33**) on the type of monodentate axial and equatorial ligands, solvent polarity, the presence of an external nucleophile, and the structure of the bidentate ligand have been considered in the literature.[117, 119–123]

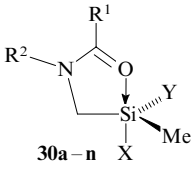
It was found that the formation of acidic impurities upon hydrolysis of pentacoordinate silicon halides has a pronounced influence on the permutation barrier: in the presence of 1,8-bis(dimethylamino)naphthalene ('proton sponge') additive, the $\Delta G^{\#}$ values of complexes **30g–i** with good leaving groups (Br, I, OTf) increase by 0.5, ~1 and 1.5 kcal mol^{-1}, respectively.[117, 121] The decrease in the $\Delta G^{\#}$ value in the series of derivatives **30e–h** occurs monotonically following the increase in the nucleofugacity of the ligand X in the series F < Cl < Br < I < OTf (Table 6).

Table 6. Activation parameters of compounds **30**–**33** in various solvents.[121, 123]

Complex	Solvent	$\Delta G^{\#}_{298}$ /kcal mol^{-1}	$\Delta H^{\#}_{298}$ /kcal mol^{-1}	$\Delta S^{\#}_{298}$ (see [a])	Complex	Solvent	$\Delta G^{\#}_{298}$ /kcal mol^{-1}	$\Delta H^{\#}_{298}$ /kcal mol^{-1}	$\Delta S^{\#}_{298}$ (see [a])
30a	$CDCl_3$	14.5	7.0	−25	**30g**	CD_3CN	14.1	5.9	−26
30b	$CDCl_3$	14.0	4.8	−31		$C_6D_5CD_3$	14.3	6.5	−26
30c	$CDCl_3$	14.3	8.0	−21	**30h**	$CDCl_3$	12.9	2.2	−31
30d	$CDCl_3$	13.0	5.4	−26		$CDCl_3$ (see [c])	13.5	4.4	−42
30e	$CDCl_3$	25.3	19.3	−20	**30i**	$CDCl_3$	12.1	3.5	−29
	$CDCl_3$ (see [b])	14.4	6.7	−26		$CDCl_3$ (see [c])	13.8	1.2	−36
30f	$CDCl_3$	14.5	6.2	−28	**30j**	$CDCl_3$	28.9	26.2	−9
	$CDCl_3$ (see [c])	14.6	5.0	−32	**30k**	$CDCl_3$	17.9	9.0	−30
	CD_2Cl_2	14.2	6.2	−27	**30l**	$CDCl_3$	15.2	3.0	−41
	$(CD_3)_2CO$	15.5	8.5	−24	**30m**	$CDCl_3$	26.9	23.3	−12
	CD_3CN	14.1	6.4	−26	**30n**	$CDCl_3$	18.42	8.6	−33
	$C_6D_5CD_3$	16.0	3.8	−29	**31a**	$CDCl_3$	10.6	13.6	10
30g	$CDCl_3$	13.7	6.2	−25	**31b**	$CDCl_3$	14.0	–	–
	$CDCl_3$ (see [c])	14.2	7.4	−23	**32a**	$CDCl_3$	9.6	13.1	12
	CD_2Cl_2	14.3	4.0	−35	**32b**	$CDCl_3$	29.4	25.8	−12
	$(CD_3)_2CO$	14.0	5.3	−29	**33**	$CDCl_3$	17.8	9.5	−28

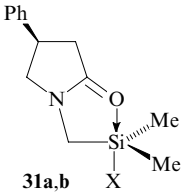
Note. Solution concentration ~0.1 mol litre^{-1}. [a] In cal mol^{-1} K^{-1}. [b] In the presence of $[Bu_4N]F \cdot 3H_2O$ (0.01 mol litre^{-1}). [c] In the presence of 1,8-bis(dimethylamino)naphthalene.

The replacement of the Me ligand in an equatorial position of TBP by a Ph group (complexes **30j**–**n**, **33**) is accompanied by increase in $\Delta G^{\#}$ by 3–4 kcal mol^{-1} opposite to the change in the O → Si bond length from 2.215 Å (compound **30f**) to 2.197 Å (compound **30n**) (see Table 6).[117, 121]

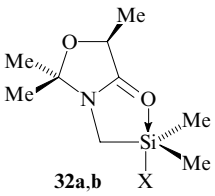


30a–**n**

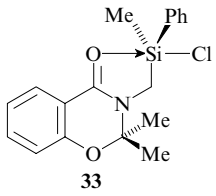
Compound **30**	R^1	R^2	X	Y
a	Me	$CHEtCH_2OAc$	Cl	Me
b	CHMeOAc	Me	Cl	Me
c	CHPhOAc	Me	Cl	Me
d	CHMeCl	Me	Cl	Me
e	Me	CHMePh	F	Me
f	Me	CHMePh	Cl	Me
g	Me	CHMePh	Br	Me
h	Me	CHMePh	I	Me
i	Me	CHMePh	OTf	Me
j	Me	Me	F	Ph
k	Me	Me	Cl	Ph
l	Me	Me	Br	Ph
m	Me	CHMePh	F	Ph
n	Me	CHMePh	Cl	Ph



31a,**b** X = Cl (**a**), $OC(O)CF_3$ (**b**).



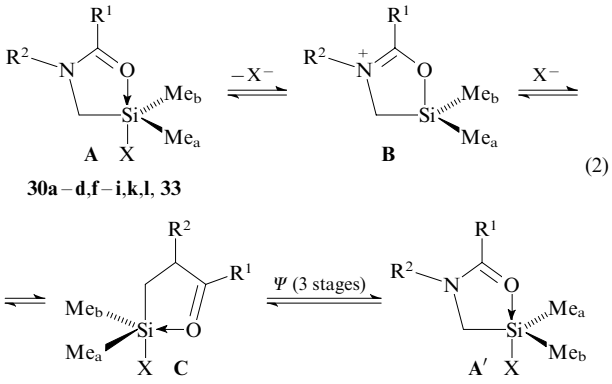
32a,**b** X = F (**a**), Cl (**b**).



33

Low permutation barriers for compounds **31a** and **32a** are due to the ease of dissociation of the relatively weak O → Si bond (2.535 Å in compound **31a**).[117, 121] The positive activation entropies indicate that the rate-determining step of the process involves a transition state structurally similar to a tetracoordinate intermediate resembling that shown for compounds **29**.

For halosilanes **30g**–**i**,**l** with good leaving monodentate ligands and for chlorosilanes with relatively short O → Si bond and elongated Si–Cl bond (complexes **30a**–**d**,**f**,**k**, **33**), the activation barrier to permutation in polar solvents is lower than in aprotic $C_6D_5CD_3$ (by 2–3 kcal mol^{-1}, see Table 6). In view of these data, a mechanism including dissociation of the Si–X bond to give a new ionic tetracoordinate intermediate **B** was proposed.[117, 121]



A **B** **C** **A′**

30a–**d**,**f**–**i**,**k**,**l**, **33** (2)

The subsequent nucleophilic attack by X^- takes place from the rear with respect to the C–Si bond and affords pentacoordinate intermediate **C**. Topomer **A′** is formed after pseudorotation in intermediate **C**. High negative activation entropy (see Table 6) may be attributed to efficient solvation of intermediate **B** by solvent molecules.[117]

Bearing in mind the found concentration dependence in the ^{19}F NMR spectra and negative activation entropies (from −10 to −20 cal mol^{-1} K^{-1}) for monofluorides **30e**,**j**,**m**, it was concluded that ligand permutation can occur *via* the formation of intermolecular associates with bridging fluorine atoms.[117, 121]

For complex **30e**, a representative of fluorosilanes having the least susceptibility for hydrolysis in the series of halosilanes, it was found that catalytic amount of CF_3CO_2H added decreases the barrier to permutational

isomerization.[124] It was shown by multinuclear (^{1}H, ^{13}C, ^{19}F, ^{29}Si) NMR that protonation of oxygen resulting in the tetracoordinate intermediate may involve either CF_3CO_2H or HF formed upon the electrophilic attack of the F atom.[117, 124]

The barrier to permutational isomerization of complexes **30**–**33** in the presence of external nucleophiles {KF, LiX (X = Cl, Br), $[Bu^n_4N]F \cdot 3H_2O$, $[Et_3NCH_2Ph]X$ (X = Cl, Br)} decreases on average by more than 10 kcal mol^{-1} (Refs 117, 119 and 125). These pronounced differences were explained in terms of associative mechanism including the formation of hexacoordinate intermediates both without cleavage of the O → Si bond (Scheme 1) and with cleavage of this bond (Scheme 2).†

† In Scheme 2 and below a popular way of designating enantiomeric TBP is used. Donor atoms are numbered arbitrarily, TBP is designated by indicating the axial ligands, for example (25). If for the look from the side of axial ligand with a smaller number, the numbers of equatorial ligands increase clockwise, these are designated by characters without the stroke, *i.e.*, (25), and if they increase counter-clockwise, by characters with a stroke, *i.e.*, ($\bar{2}\bar{5}$).

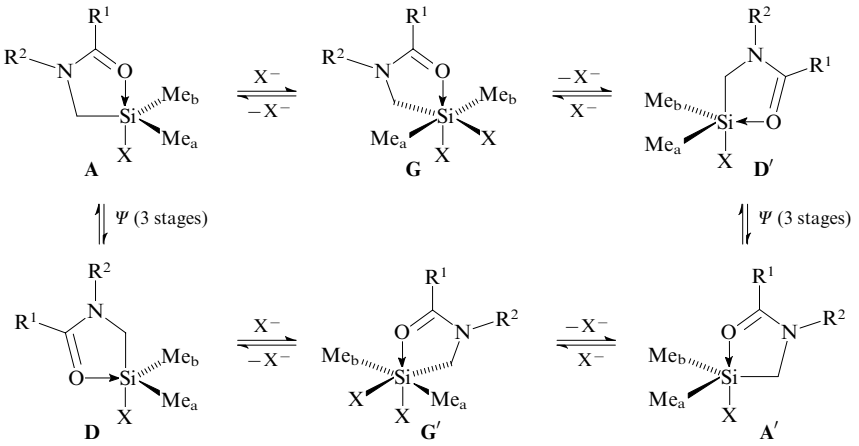
In the former case, the exchange of diastereotopic methyl groups Me_a and Me_b can proceed through a frontal (with respect to oxygen) attack of Si by the nucleophile from the side opposite to the CH_2 group of the chelating ligand (**A** ⇄ **G**). The subsequent elimination of the halide ion from the axial position in hexacoordinate intermediate **G** and pseudorotation in pentacoordinate intermediate **D′** results in topomer **A′**.

The second mechanism (with cleavage of the O → Si bond, see Scheme 2) may involve intermediate adducts with either one nucleophilic species (**I**: **A** ⇄ **I** ⇄ **I′**) or with two species (**H**: **A** ⇄ **G** ⇄ **H** or **A** ⇄ **I** ⇄ **H**) and so on. The probability of pseudorotation along the route **I** ⇄ **I′** is high because all ligands are monodentate in this case.[117, 119, 125]

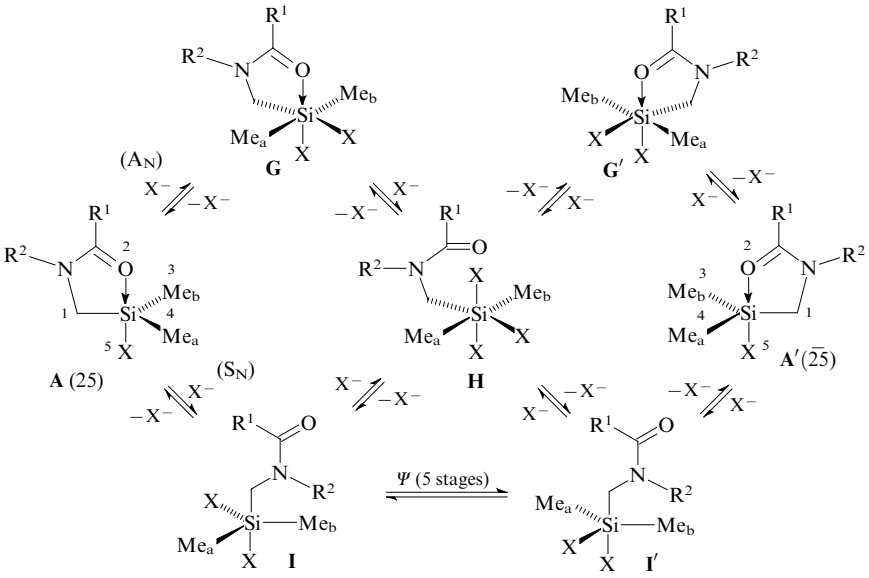
b. Complexes with several electron-acceptor substituents

The much lower barrier to the process resulting in position exchange of fluorine atoms in monochelate pentacoordinate di- and trifluorosilanes **34**–**37** (9–11 kcal mol^{-1}, Table 7) compared with the barrier to the exchange of methyl groups in monofluorosilanes (> 20 kcal mol^{-1}, see Table 6) is attributed to differences in permutation mechanisms.[117, 126–128] Low activation barriers are also typical of

Scheme 1



Scheme 2



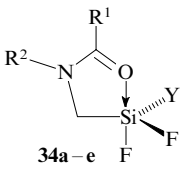
A_N is nucleophilic addition; S_N is nucleophilic substitution.

Table 7. Activation parameters of ligand exchange in polyfluorides **34**–**37** (in $CDCl_3$).[117, 126–128]

Complex	$\Delta G^{\#}_{298}$ (see [a])	$\Delta H^{\#}_{298}$ (see [a])	$\Delta S^{\#}_{298}$ (see [b])	$\Delta G^{\#}_{c}$ (see [a])	T_c /°C
34a	9.6	11.3	−5	9.9	−76
34b	9.9	13.0	−10	10.2	−70
34c	9.7	12.1	−7	9.7	−78
34d	9.6	10.8	−2	9.8	−75
34e	9.3	11.1	−6	9.4	−76
35a	9.7	11.2	−4	9.6	−74
35b	9.8	10.2	−4	9.9	−75
35c	–	–	–	9.6	−73
35d	–	–	–	~9.5	–
36	9.9	13.3	−8	9.9	−72
37	9.7	10.9	−4	10.0	−71

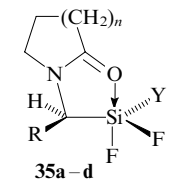
[a] In kcal mol^{-1}; [b] in cal mol^{-1} K^{-1}.

ligand exchange in complex **38** (10.2 kcal mol^{-1}, $T_c = -8$ °C).[129]



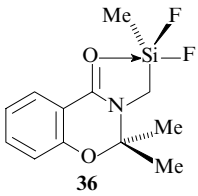
34a–**e**

Y = Me: R^1 = Ph, R^2 = H (**a**),
$R^1 = R^2$ = Me (**b**);
R^1 = Me: R^2 = Me, Y = F (**c**);
R^2 = CHMePh, Y = Me (**d**);
R^2 = CHMePh, Y = F (**e**).

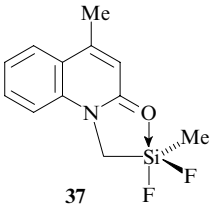


35a–**d**

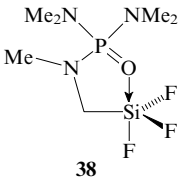
R = H, Y = Me, n = 3 (**a**);
R = H, Y = F: n = 1 (**b**), 2 (**c**);
R = Me, Y = F, n = 1 (**d**).



36



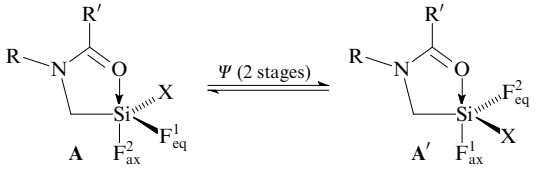
37



38

The permutation entropy in polyfluorides **34**–**37** is smaller in magnitude than analogous values for monofluorides (see Table 6). In the concentration range studied (0.02–0.3 mol $litre^{-1}$), the activation parameters for polyfluorides are roughly the same within the accuracy of measurements irrespective of the structure. This attests to predominantly intramolecular character of the process.[117, 126–128]

According to X-ray diffraction data, on going from monofluoride **30e** to difluoride **34d** and then to trifluoride **34e**, the O → Si bond length decreases: 2.149, 2.016 and 1.898 Å, respectively.[117, 130] A dissociative mechanism involving the 'open' intermediate like **D** for complex **12d** should have resulted in an increase in $\Delta G^{\#}$ values in this series, which contradicts experimental data. The **A** ⇄ **A′** mechanism without silicon inversion including two pseudorotation steps, which is equivalent to turnstile rotation as regards the stereochemical outcome, is more likely.[117]

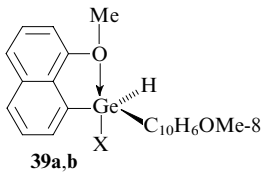


A **A′**

This conclusion is supported by X-ray diffraction data indicating similar geometric structures of the distorted TBP and the transition state of turnstile rotation (the $F^1_{eq}-Si-X$ angle is 98–100°) in the polyfluorides in question.[117, 130]

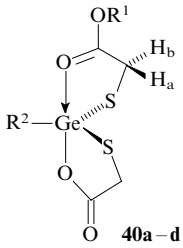
4. Complexes with O → M (M = Ge, Sn) coordination bond

Unlike chelates of pentacoordinate silicon, the stereochemical non-rigidity of analogous derivatives of germanium and tin with O → M bond (M = Ge, Sn) is much less studied. Published data on stereodynamic processes in complexes **39**–**42** known to date are summarized in Table 8.[131–133]



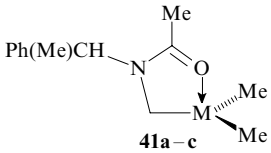
39a,**b**

X = OTf (**a**), I (**b**).



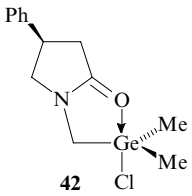
40a–**d**

R^1 = H: R^2 = Bu^t (**a**), Ph (**b**);
R^1 = NHC_6H_5: R^2 = Bu^t (**c**), Ph (**d**).



41a–**c**

M = Ge: X = Cl (**a**), Br (**b**);
M = Sn, X = Cl (**c**).



42

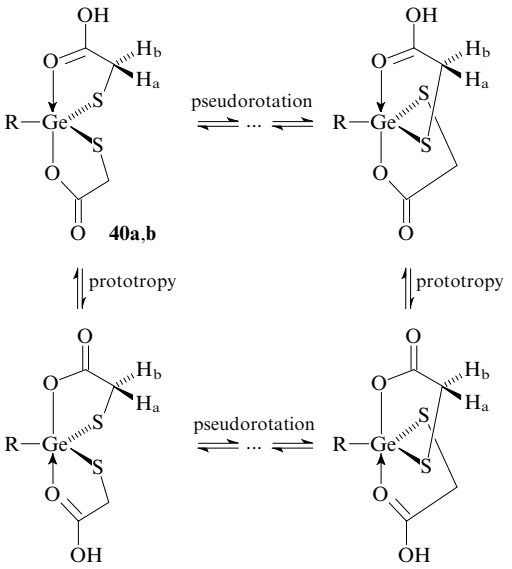
Table 8. Activation parameters of permutation for complexes **39**–**42**.[117, 131–133]

Complex	Solvent	$\Delta G^{\#}$ (see [a])	$\Delta H^{\#}$ (see [a])	$\Delta S^{\#}$ (see [b])	T_c /°C
39a	$CDCl_3$	10.5	–	–	−50
39b	$CDCl_3$	10.8	–	–	−41
40a	$(CD_3)_2CO$	12.2	–	–	−23
40b	$(CD_3)_2CO$	12.4	–	–	−25
40c	$CD_2Cl_2 + CS_2$ (2 : 1)	12.1	–	–	−34
40d	CD_2Cl_2	11.6	–	–	−39
41a	CD_3CN	22.0	4.6	−25	>70
41b	CD_3CN	17.0	10.6	−22	67
41c	$CDCl_3$	25.1	17.3	−26	>60
42	$CDCl_3$	17.6	12.6	−16	50

[a] In kcal mol^{-1}; [b] in cal mol^{-1} K^{-1}.

For the process responsible for averaging of the signals of indicator groups in complexes **40**, a mechanism was proposed according to which the coordination bond is not cleaved but a prototropic shift and subsequent pseudorotation at the germanium TBP take place (Scheme 3).[132]

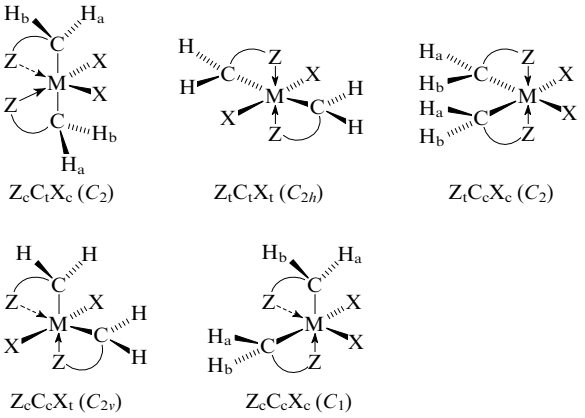
Scheme 3



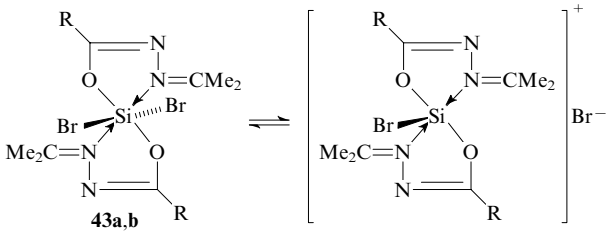
In view of the great negative activation entropies of permutational isomerization (down to -26 cal mol^{-1} K^{-1}) for complexes **41** and **42**, a mechanism including dissociation of the M–Hal bond with subsequent effective solvation of particles in the transition state similar to mechanism (2) was proposed.[117]

III. Neutral hexacoordinate complexes of tetravalent elements

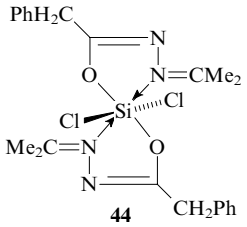
Octahedral bis-chelate complexes with Z → M intramolecular coordination bond (M = Si, Ge, Sn; Z is the oxygen or nitrogen donor atom in bidentate C,Z-chelating ligand) can *a priori* exist as five diastereomers (the notation $Z_cC_cX_t$ means, for example, that pairs of Z and C atoms are *cis*- and X atoms are *trans*-arranged) (Hereinafter the dashed arrows designate coordination bonds directed backward beyond the page.)



According to X-ray diffraction data, a pair of monodentate ligands in neutral bis-chelate complexes of hexacoordinate silicon,[7,38,134–136] germanium and tin[11,12,137] occupy mainly the *cis*-position with respect to each other. However, there are some exceptions: bulky monodentate ligands, for example, Br and Cl atoms in complexes **43a**,**b**,[138] **44** [139] and $[(AcN(Me)CH_2)_2SiCl]^+Cl^-$ (Ref. 140) occupy sterically more favourable *trans*-positions with respect to each other.

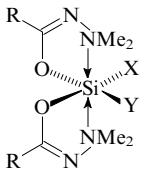


R = $PhCH_2$ (**a**), Ph (**b**).

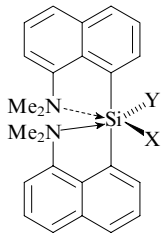


1. Complexes with N → M coordination bond (M = Si, Ge)

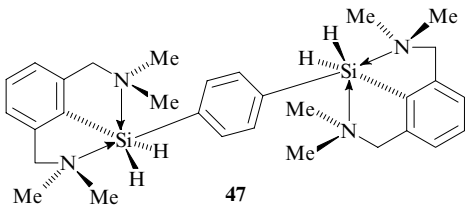
An early study devoted to the use of NMR for investigation of the structure of neutral complexes of chiral hexacoordinate silicon described the dependence of the rate of permutation and/or intermolecular exchange processes on the structure of bi- and monodentate ligands at the central atom.[141] This study dealt with compounds **45d**,**l**. Later, the stereodynamic processes in the coordination unit of similar complexes **46**–**48** were studied by DNMR.[142–156]

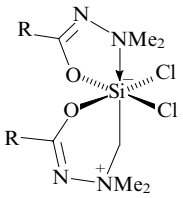


X = H, Y = Cl: R = Me (**a**), Ph (**b**), CF_3 (**c**); X = Me, Y = Cl: R = Me (**d**), Ph (**e**), CF_3 (**f**), Bu^t (**g**); X = Ph, Y = Cl: R = Me (**h**), Ph (**i**), CF_3 (**j**), CH_2Ph (**k**); X = Y = Cl: R = Me (**l**), Ph (**m**), CF_3 (**n**); X = R = Ph, Y = F (**o**); X = cyclo-C_6H_{11}, Y = Cl, R = CF_3 (**p**).



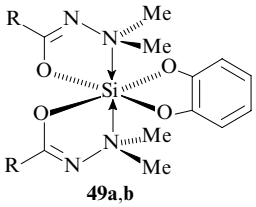
X–Y = 1,2-$O_2C_6H_4$ (**a**); X = H: Y = OMe (**b**), F (**c**), Me (**d**); X = Me, Y = Ph (**e**).



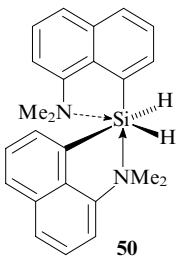


48a–c R = H (**a**), Ph (**b**), CF_3 (**c**).

The activation barriers to stereodynamic processes in the coordination units of complexes **45**;[39, 142–144] **46**, **47**;[145–147] **48**, **49** [139, 148–155] determined by DNMR are presented in Table 9.



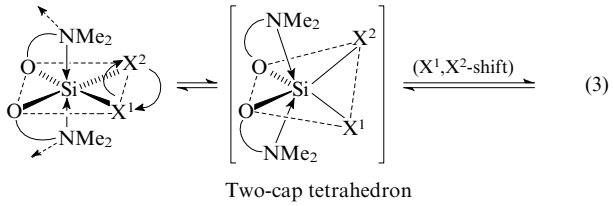
49a,**b** R = Ph (**a**), (*RS*)-CH(Me)Ph (**b**).



50

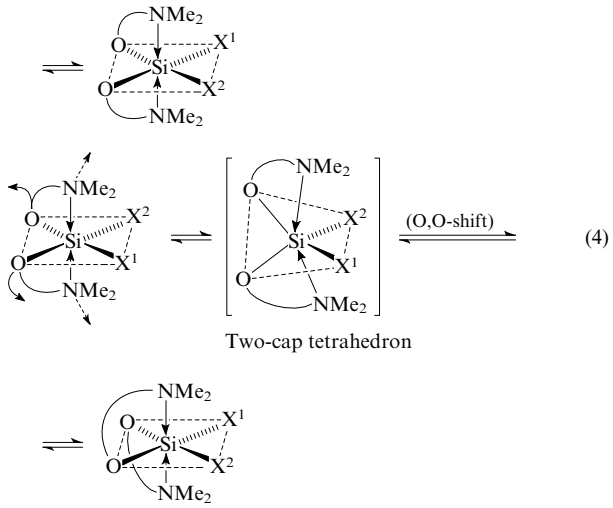
The patterns of variation of NMR spectra depending on temperature clearly demonstrated that in the coordination unit of some studied complexes, two stereodynamic processes take place (with activation barriers of $\Delta G_1^{\#}$ and $\Delta G_2^{\#}$, respectively). (For more symmetrical complexes, for example, **45l–n**, **49a**, only one process takes place.) On the basis of analysis of spectral parameters, it was concluded that the first of two processes occurs *via* reversible dissociation of the N → Si bond without silicon inversion.[142, 143] Weakening of the intramolecular coordination bond as a result of additional coordination of Si to an external nucleophile molecule, for example, CD_3NO_2, is accompanied by a decrease in the first activation barrier by more than 3–4 kcal mol^{-1}, whereas the second barrier remains almost unchanged. In the researchers' opinion, this supports the dissociative mechanism.

For the second process with a higher activation energy (15–20 kcal mol^{-1}, see Table 9), a regular 1,2-shift mechanism was proposed; this includes the formation of a two-cap tetrahedral transition state or intermediate with two covalent and two coordination bonds N → Si followed by position exchange of either monodentate ligands (X^1,X^2-shift) or oxygen atoms of the chelate rings (O,O-shift).[142, 143]



(3)

Two-cap tetrahedron



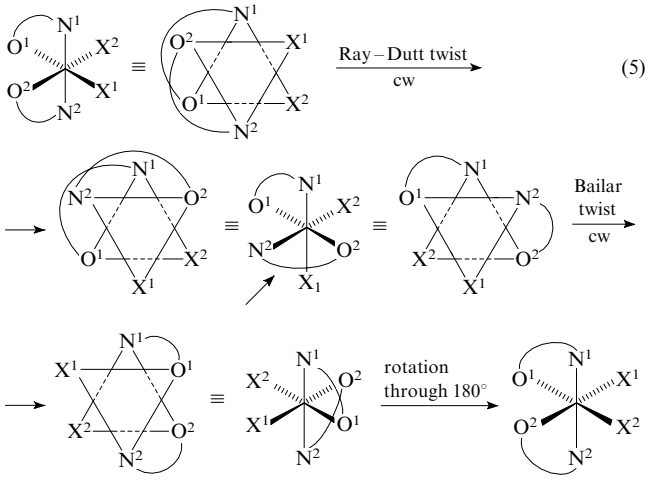
(4)

Two-cap tetrahedron

The authors state three arguments in favour of 1,2-shift mechanism.[148] First, topomerization according to the Bailar or Ray–Dutt mechanism requires at least two twists [mechanisms (5) and (6)] unlike 1,2-shift. Second, two successive twists do not account for the occurrence of two stereodynamic processes. Finally, the proposed mechanisms (3) and (4) are indirectly supported by X-ray diffraction data for some chelates (for example, for compounds **47** and **50**) having a two-cap tetrahedron structure in the crystalline state.[145, 147]

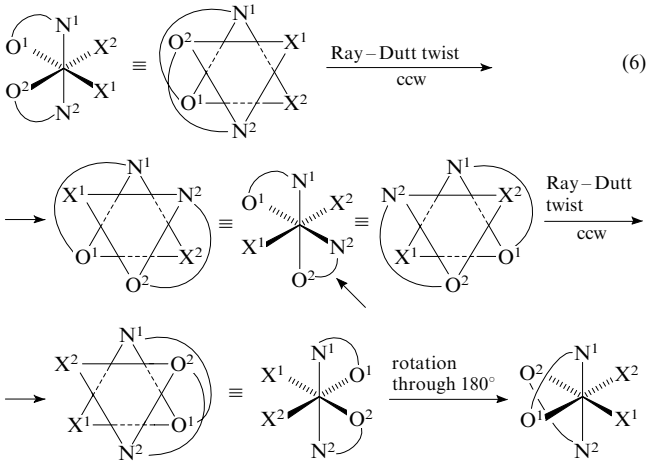
Table 9. Activation free energy of exchange in complexes **45–49**.[139, 142, 143, 145–155]

Complex	Solvent	$\Delta G_1^{\#}$ /kcal mol^{-1}	$\Delta G_2^{\#}$ /kcal mol^{-1}	Complex	Solvent	$\Delta G_1^{\#}$ /kcal mol^{-1}	$\Delta G_2^{\#}$ /kcal mol^{-1}
45a	$C_6D_5CD_3$	17.0	17.8	**45o**	$CDCl_3$	15.8	15.9
45b	$C_6D_5CD_3$	17.5	18.5	**46a**	$CDCl_3$	20.5	–
45c	$C_6D_5CD_3$	17.5	18.0	**46b**	$CDCl_3$	15.2	–
45d	$C_6D_5CD_3$	13.8	14.8	**46c**	$CDCl_3$	14.7	–
45e	$C_6D_5CD_3$	13.7	14.8	**46d**	$CDCl_3$	9.3	–
45f	$C_6D_5CD_3$	13.7	14.6	**46e**	$CDCl_3$	12.7	–
45h	$C_6D_5CD_3$	15.9	16.9	**47**	$CDCl_3$	8.4	11.5
45i	$C_6D_5CD_3$	15.8	16.4	**48a**	$C_6D_5CD_3$	15.8	16.7
	CD_3NO_2	10.6	16.0		$CDCl_3$	13.6	15.0
45j	$C_6D_5CD_3$	15.9	16.3	**48b**	$C_6D_5CD_3$	17.4	18.8
45k	$C_6D_5CD_3$	15.9	16.9	**48c**	$C_6D_5CD_3$	16.6	21.2
45l	$C_6D_5NO_2$	17.9	–		$C_6D_5NO_2$	16.8	> 20.0
45m	$C_6D_5NO_2$	19.5	–	**49a**	$CDCl_3$	21.1	–
45n	$C_6D_5NO_2$	20.5	–	**49b**	$CDCl_3$	15.7	17.0



(5)

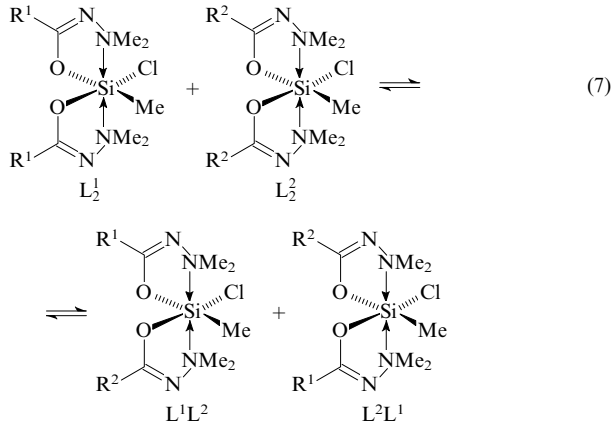
cw is clockwise; ⟶ is gaze direction.



(6)

ccw is counterclockwise; ⟶ is gaze direction.

An unusual exchange of chelating ligands takes place on mixing of equimolar amounts of two different complexes out of compounds **45e**,**g**,**h**,**p** in $C_6D_5CD_3$ or $CDCl_3$.[156]



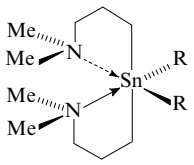
(7)

The low-temperature spectra exhibited four sets of signals assigned to two initial structures (L_2^1, L_2^2) and two mixed bis-chelates (L^1L^2 and L^2L^1).[156] On warming-up to room temperature, the latter signals are broadened and coalesce into an averaged set. The activation barrier to this process for mixed complexes **45e** + **45p** was 14.7 kcal mol^{-1} (Ref. 156).

The ^{1}H NMR spectrum of the complex $PhGe(OCH_2CH_2NMe_2)_2Cl$ depends on temperature.[157–159] The observed two sets of signals correspond, in the authors' opinion, to neutral and ionic $[PhGe(OCH_2CH_2NMe_2)_2^+Cl^-]$ species present in solution in a dynamic equilibrium.

2. Complexes with N → Sn coordination bond

Complexes **51a**–**d** were found to undergo ligand exchange whose activation parameters were calculated at the coalescence temperature of NMe_2 signals.[160]

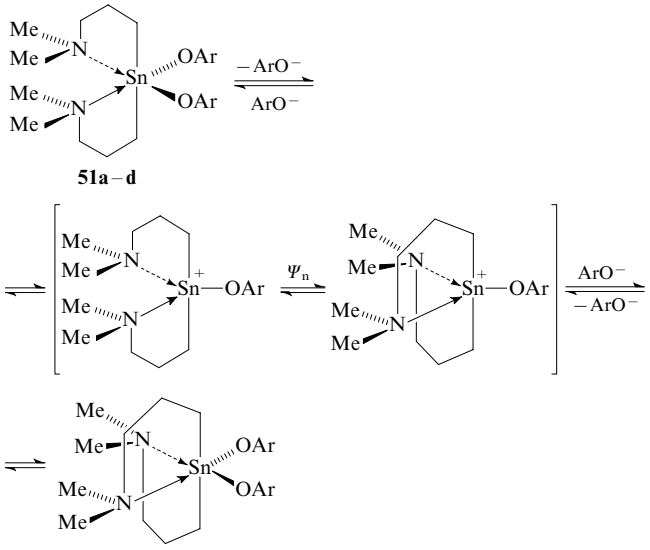


51a–**e**

R = OPh (**a**), $OC_6H_4Bu^t$-4 (**b**), $OC_6H_4NO_2$-4 (**c**), OC_6H_4F-2 (**d**), SPh (**e**).

Complex	$\Delta G^{\#}$/kcal mol^{-1}
51a	11.7
51b	12.6
51c	11.2
51d	15.2

Since $^2J_{SnOC}$ disappears from the ^{119}Sn NMR spectra, a permutation mechanism comprising cleavage of the covalent Sn–O bond followed by multistep pseudorotation in the resulting TBP cation was proposed for such complexes.[160]

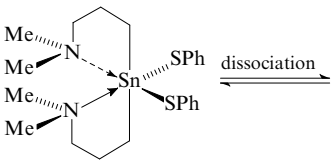


51a–**d**

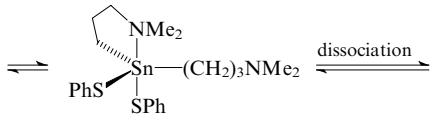
The increase in the chemical shift of the ^{119}Sn NMR signal of complex **51a** with an increase in temperature is slight, whereas the ^{119}Sn NMR signal of complex **51e** undergoes considerable downfield shift in the same temperature range, as typical of tetracoordinate tin.[160]

Complex	T/°C	$\delta(^{119}Sn)$/ppm
51a	+30	−245
	−50	−257
51e	+30	1.70
	−50	−45.3

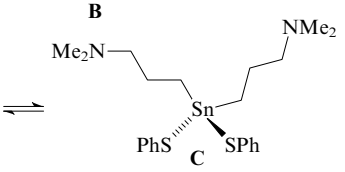
Relying on this, it was concluded [160] that complex **51e** tends to undergo fast (on the NMR time scale) exchange between hexa- (**A**), penta- (**B**) and tetracoordinate (**C**) structures.



51e (**A**)

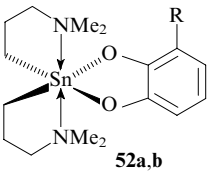


B



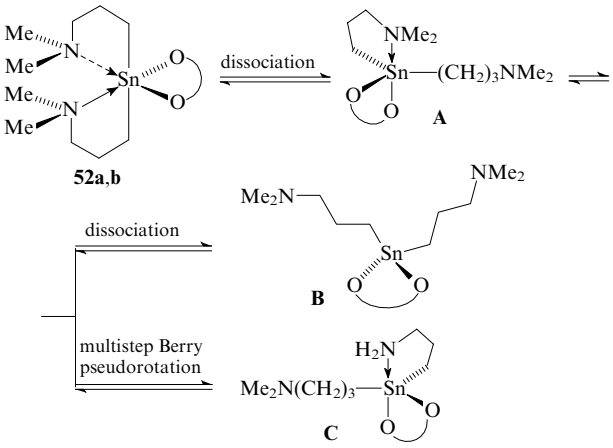
C

For explaining the stereodynamic process ($\Delta G^{\#} = 11.8$ kcal mol^{-1}) taking place in complexes **52a**,**b**



52a,**b** R = H (**a**), OMe (**b**).

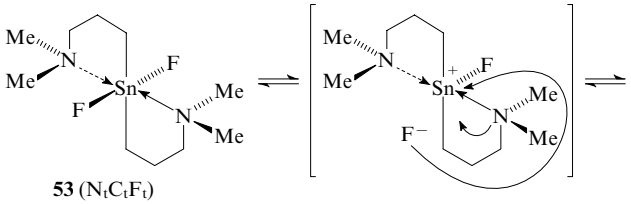
and resulting in equivalence of NMe_2-group signals, two mechanisms were proposed.[160]



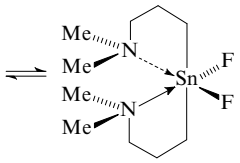
Cleavage of the N → Sn bond results in pentacoordinate intermediate **A** with two O—Sn covalent bonds. This is followed by either dissociation of the second N → Sn bond to give structure **B** or by multistep pseudorotation giving rise to structure **C**. The latter mechanism is supported by the fact that calculated activation energy for enantiomerization for complex **52a** (11.8 kcal mol^{-1}) does not differ, to within the error, from the activation barriers for complexes **51a**–**c** (11.2–12.6 kcal mol^{-1}) for which a similar ligand exchange mechanism has been proposed. The activation parameters of enantiomerization for complex **52b** have not been determined. However, the similarity of structures of compounds **52a** and **52b** suggests similar mechanisms for ligand exchange in them.

For some pentacoordinate complexes of silicon (see Section II.3), it was shown that dissociation of relatively weak O → Si bond has a lower barrier than pseudorotation (~10 and ~13–14 kcal mol^{-1}, respectively). Therefore, low activation barriers to enantiomerization in complexes **51**, **52** with activation entropy being unknown rather correspond, in our opinion, to the dissociative mechanism with reversible cleavage of the intramolecular coordination bond and inversion of the central atom in the TBP intermediate.

Difluoride **53** existing in the solid state as a single isomer with the $N_tC_tF_t$ geometry was found to occur in solution as a dynamic equilibrium of diastereomers $N_tC_tF_t$ (80%) and $N_cC_tF_c$ (20%).[161]



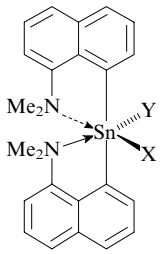
53 ($N_tC_tF_t$)



$N_cC_tF_c$

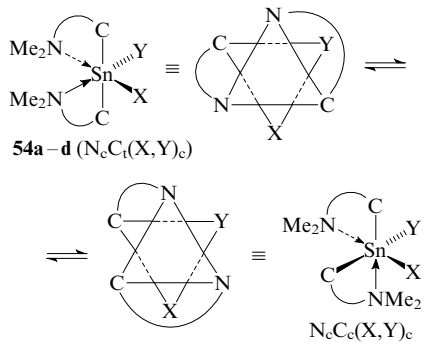
The behaviour of the spin-spin coupling constants $^3J(^{119}Sn \leftarrow NCH)$ through the intramolecular coordination bond for both fast and slow, on the NMR time scale, exchange processes and disappearance of the spin-spin coupling constant $^1J(^{119}Sn-F)$ at high temperatures led to the conclusion that the N → Sn coordination in complex **53** is retained upon diastereomerization.[161] Elimination of the fluoride ion yields a pentacoordinate intermediate, which is then attacked in the *cis*-position with respect to another fluorine atom. Note that diastereomerization in the *cis*-isomer $N_cC_tF_c$ should be accompanied by enantiomerization; however, the authors [161] did not consider this probability.

Unlike symmetric structure **54a**, complexes **54b**–**d** with different monodentate ligands exist in solution at low temperatures as two hexacoordinate isomers in a slow dynamic equilibrium.[162]



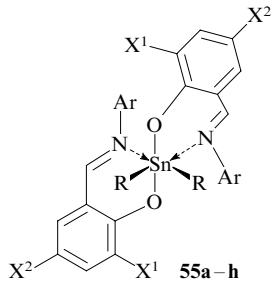
54a–**d** X = Y = Cl (**a**); Y = I: X = Me (**b**), Et (**c**); X = Br, Y = Ph (**d**).

One of these has two linear X(Y)—Sn ←NMe_2 fragments and *trans*-arrangement of carbon atoms, while the other has *cis*-configuration. The conclusion about non-dissociative reaction mechanism was based on the retention of the spin-spin coupling constant $^3J(^{119}Sn \leftarrow NCH)$ on fast exchange.[163]



54a–d ($N_cC_t(X,Y)_c$)

The ^1H NMR spectra of complexes **55a**,**g**,**h** show a single set of signals. Conversely, in solutions of complexes **55b–e**, an equilibrium involving two isomers, slow on the NMR time scale, was found.[163,164] In the authors' opinion, the structure of one of these corresponds to $N_cO_tR_c$, that of the other, to $N_cO_cR_c$. Note that the absence of a temperature dependence of the signals of one of the forms of complex **55c**, as follows from temperature-dependent ^1H NMR spectrum,[163] can be attributed to the equilibrium $N_cO_tR_c \rightleftarrows N_tO_tR_t$.



55a–h

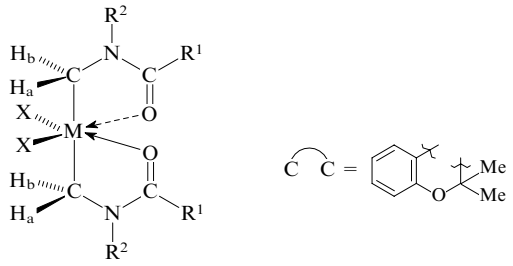
Ar = Ph, $X^1 = X^2$ = Cl:
R = Me (**a**), CH_2Ph (**b**);
Ar = Ph, X^1 = Bu^t, X^2 = H:
R = Me (**c**), CH_2Ph (**d**), Bu^n (**e**);
Ar = C_6F_5, X^1 = Bu^t,
X^2 = H: R = Me (**f**), CH_2Ph (**g**), Bu^n (**h**).

3. Complexes with O → M coordination bond (M = Si, Ge, Sn)

a. Complexes with a five-membered chelate ring

The structure and stereochemical non-rigidity of complexes with the O → M bond (M = Si, Ge, Sn) have now been studied in considerable detail.[165–175] In the coordination unit of these complexes, two stereodynamic processes take place: enantiomerization and diastereomerization.

Enantiomerization. The activation parameters of permutational isomerization in the coordination unit of bischelates **56–58** are presented in Table 10.



56a–c, **57a–m**, **58a–m**

56: M = Si, X = F: $R^1 = R^2$ = Me (**a**); R^1 = Me, R^2 = CHMePh (**b**); R^1-R^2 = C C (**c**).

57: M = Ge, X = F: $R^1-R^2 = (CH_2)_n$ [n = 3 (**a**), 4 (**b**), 5 (**c**)), C C (**d**); X = Cl: $R^1 = R^2$ = Me (**e**); $R^1-R^2 = (CH_2)_n$ [n = 3 (**f**), 4 (**g**), 5 (**h**)], C C (**i**); X = Br: $R^1 = R^2$ = Me (**j**); $R^1-R^2 = (CH_2)_n$ [n = 1 (**k**), 2 (**l**), 3 (**m**)].

58: M = Sn, X = F: $R^1-R^2 = (CH_2)_n$ [n = 3 (**a**), 4 (**b**), 5 (**c**)]; X = Cl: $R^1 = R^2$ = Me (**d**), $R^1-R^2 = (CH_2)_n$ [n = 3 (**e**), 4 (**f**), 5 (**g**)]; X = Br: $R^1-R^2 = (CH_2)_n$ [n = 3 (**h**), 4 (**i**), 5 (**j**)]; X = I: $R^1-R^2 = (CH_2)_n$ [n = 3 (**k**), 4 (**l**), 5 (**m**)].

Table 10. Activation parameters of enantiomerization of compounds **56–58**.[117,171–174]

Complex	Solvent	$\Delta G^{\#}_{298}$ /kcal mol^{-1}	$\Delta H^{\#}_{298}$ /kcal mol^{-1}	$\Delta S^{\#}_{298}$ (see [a])	Complex	Solvent	$\Delta G^{\#}_{298}$ /kcal mol^{-1}	$\Delta H^{\#}_{298}$ /kcal mol^{-1}	$\Delta S^{\#}_{298}$ (see [a])
56a	$CDCl_3$	13.5	15.2	6	**57l**	$CDCl_3$	12.1	14.0	5
56b	$CDCl_3$	16.5	19.0	9	**57m**	$CDCl_3$	12.6	14.2	6
56c	$CDCl_3$	16.4	19.2	9		CD_3CN	12.9	13.8	3
57a	$CDCl_3$	12.1	13.3	4	**58a**	$CDCl_3$	13.8	15.6	6
57b	$CDCl_3$	13.9	16.6	5	**58b**	$CDCl_3$	13.7	15.8	7
57c	$CDCl_3$	13.6	15.6	5	**58c**	$CDCl_3$	14.0	16.9	10
57d	$CDCl_3$	15.3	16.8	5	**58d**	$CDCl_3$	13.6	13.9	1
57e	$CDCl_3$	12.1	13.2	4		$(CD_3)_2CO$	10.2	12.0	6
57f	$CDCl_3$	10.6	12.2	7	**58e**	$CDCl_3$	13.6	13.9	1
57g	$CDCl_3$	12.8	16.9	15		$CDCl_3$ (see [c])	13.5	14.1	2
57h	$CDCl_3$	13.6	18.2	15	**58f**	$CDCl_3$	13.8	14.9	4
	$CDCl_3$ (see [b])	13.4	18.0	16	**58g**	$CDCl_3$	13.8	14.7	3
	CD_3CN	13.6	17.0	12	**58h**	$CDCl_3$	13.5	13.9	1
	$(CD_3)_2CO$	13.3	17.8	15	**58i**	$CDCl_3$	13.8	14.8	3
	$C_6D_5CD_3$	13.3	18.3	17	**58j**	$CDCl_3$	13.7	14.9	4
	$(CD_3)_2CO$	14.0	15.2	4	**58k**	$CDCl_3$	12.6	12.9	1
57i	$CDCl_3$	13.6	14.9	4		CD_3CN	12.7	16.2	11
57j	$CDCl_3$	11.9	14.3	8	**58l**	$CDCl_3$	13.8	14.6	3
57k	$CDCl_3$	10.0	11.2	4	**58m**	$CDCl_3$	13.8	14.5	2

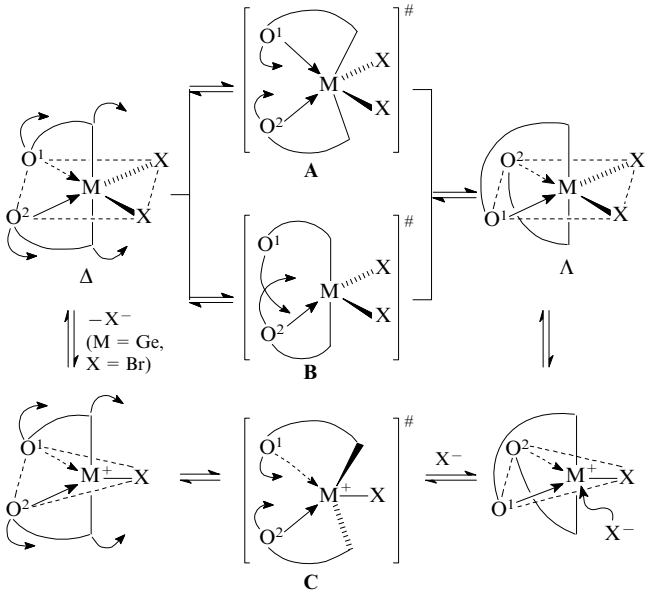
Note. Solution concentration ~0.03 mol litre^{-1}. [a] In cal mol^{-1} K^{-1}. [b] In this case, the concentration was ~0.8 mol litre^{-1}. [c] In the presence of $[Et_3NCH_2Ph]Cl$.

Depending on the nature of the central atom and the halogen atom and the structure of the bidentate ligand, the barrier to ligand exchange in bischelate hexacoordinate Si, Ge and Sn complexes varies from 10 to 16 kcal mol^{-1}. The highest $\Delta G^{\#}$ values are charecteristic of silicon difluorides **56b**,**c**.

In dihalogermanes **57a**–**m**, the barrier to permutation decreases by 1–2 kcal mol^{-1} on going from difluorides to dichlorides and then to dibromides. A similar dependence of $\Delta G^{\#}$ on the nucleofugacity of a monodentate ligand was also found for neutral monochelates (see Section II.3). The highest $\Delta S^{\#}$ value was found for germanium dichlorides **57g**,**h** (see Table 10). Among bischelates with $R^1-R^2 = (CH_2)_n$, dihalogermane complexes **57a**,**f**,**k** with the weakest O → Ge bond have the lowest barriers to permutation (~10 kcal mol^{-1}).[117, 167, 174, 176] A similar trend of variation of $\Delta G^{\#}$ as a function of the ring structure is also characteristic of neutral complexes of pentacoordinate silicon (see Section II.3).

The scheme proposed for description of the enantiomerization in bis-chelates **56**–**58** comprises either formation of two-cap transition state **A** or reversible dissociation of the O → M bond, resulting, in the case of relatively long bond, in pentacoordinate transition state **B** followed by pseudorotation in this transition state (Scheme 4).[117, 171]

Scheme 4



The higher electrical conductivity of complex **57m** compared with dichlorogermane **57h** (~3220 and 100 mS cm^2 mol^{-1}, respectively [117, 175, 176]) and the decrease in the activation entropy on going from dibromides to dichlorides (see Table 10) imply that enantiomerization may also proceed through the M–X bond dissociation step (structure **C**, see Scheme 4).[117] Note that transformations $\Delta \rightleftarrows \mathbf{A} \rightleftarrows \Lambda$ and $\Delta \rightleftarrows \mathbf{B} \rightleftarrows \Lambda$ generally resemble the 1,2-shift pattern for the permutation mechanism in the complexes of hexacoordinate silicon [mechanisms (3) and (4)].

Diastereomerization. Dynamic equilibrium with participation of diastereomers $O_cC_tBr_c$ and $O_tC_tBr_t$ slow on the NMR time scale was found in solutions of dibromogermane complexes **57j**–**m**; its activation and thermodynamic parameters are given in Table 11.[117, 171, 174] The activation barriers to diastereomerization are higher than the enantiomerization barriers in the complexes L_2GeHal_2 (see Table 10). In view of this fact and the opposite sign of activation entropy change compared to that for enantiomerization, a mechanism starting with dissociation of the Ge–Br bond was proposed for diastereomerization (Scheme 5).

Table 11. Activation and thermodynamic parameters of diastereomerization in complexes **57j**–**m**.[117]

Complex	$\Delta G^{\#}_{298}$ (see [a])	$\Delta H^{\#}_{298}$ (see [a])	$\Delta S^{\#}_{298}$ (see [b])	ΔG°_{298} (see [a])	ΔH°_{298} (see [a])	ΔS°_{298} (see [b])
57j	16.0	7.5	−28	1.0	0	3
57k	15.8	14.5	−4	0.5	−0.9	−5
57l	15.7	13.3	−8	0.1	−1.8	−6
57m	15.5	13.6	−6	0.1	−1.9	−6

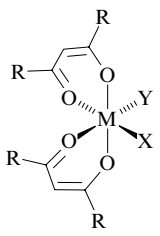
[a] In kcal mol^{-1}; [b] in cal mol^{-1} K^{-1}.

Data on the high electrical conductivity of dibromides in solution [117, 175, 176] are in agreement with Ge–Br bond dissociation to give pentacoordinate germylium ion (structure **B**) in the step preceding the rate-limiting step. The subsequent attack by the Br atom from the rear in the rate-limiting step may occur as reaction with either dibromide molecule (**A**) ($\mathbf{B} + \mathbf{A} \rightleftarrows \mathbf{ABC} \rightleftarrows \mathbf{C} + \mathbf{B}$) or free halide ion ($\mathbf{B} \rightleftarrows \mathbf{BC} \rightleftarrows \mathbf{C}$). The process $\mathbf{B} \rightleftarrows \mathbf{BD} \rightleftarrows \mathbf{D} \rightleftarrows \mathbf{DC} \rightleftarrows \mathbf{C}$ including pseudorotation in an intermediate ($\mathbf{B} \rightleftarrows \mathbf{BD} \rightleftarrows \mathbf{D}$) was considered as an alternative.[117] Note that negative activation entropies of diastereomerization may also be caused by effective solvation of the pentacoordinate cation formed as a result of reversible dissociation of the O → Ge bond.[117, 172]

Intermolecular exchange. In the case of solutions of mixtures (1 : 1) of complexes of dihalostannanes L_2SnX_2 and L_2SnY_2 (**58a**–**m**) with various monodentate ligands, the ^{119}Sn NMR spectra exhibit an additional signal apart from the signals of two initial compounds with a chemical shift equal to the arithmetic mean between the $\delta(^{119}Sn)$ values of the single dihalides. This led to the conclusion that the additional signal is due to the mixed dihalide L_2SnXY.[117] Experimental data attest in favour of retention of mutual *cis*-arrangement of the monodentate ligands in the coordination unit of mixed dihalides, which distinguishes them from the Si and Ge analogues. These differences are caused by the nature of the central atom and, first of all, its size: the *cis*-arrangement of two monodentate ligands is sterically more favourable for the tin atom, which is larger than the germanium atom.

b. Complexes with a six-membered chelate ring

The calculated values for activation free energy, enthalpy and entropy for diacetylacetonate complexes of silicon **59a**,**b**,[177, 178] germanium **60** [177–179] and tin **61a**–**d** [180–182] are summarized in Table 12.



59a,**b**; **60**; **61a**–**d**

59: M = Si: X = Cl, Y = Ph, R = Me (**a**);
X = Y = Bu^{t}O, R = Bu^t (**b**);
60: M = Ge, X = Cl, Y = Ph, R = Me;
61: M = Sn, R = Me: X = Cl, Y = Ph (**a**);
X = Y = Ph (**b**), Cl (**c**);
X = Me, Y = Cl (**d**).

Scheme 5

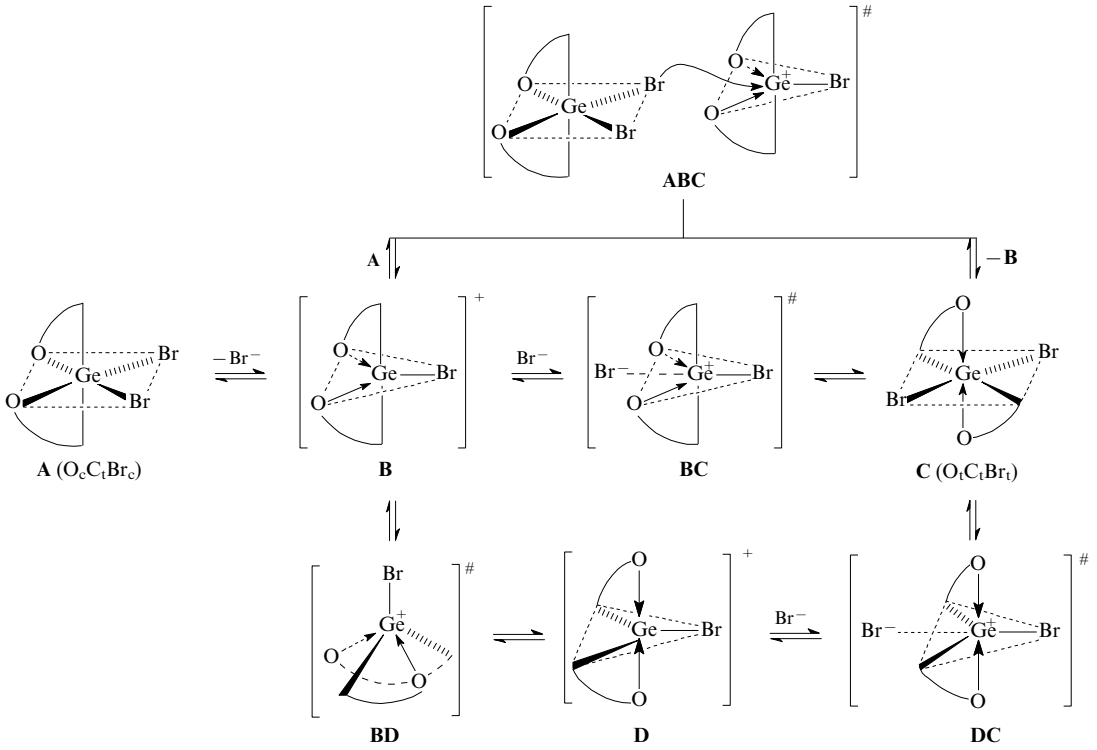


Table 12. Activation parameters of ligand exchange in complexes **59**–**61**.[177–182]

Complex	Solvent	$\Delta G^{\#}_{298}$ /kcal mol^{-1}	$\Delta H^{\#}_{298}$ /kcal mol^{-1}	$\Delta S^{\#}_{298}$ (see [a])
59a	$CDCl_3 + CCl_4$	13.1	6.4	−22
59b	C_6D_6	14.4	—	—
60	$CDCl_3 + CCl_4$	16.6	12.8	−13
61a	$CDCl_3$	16.6	12.2	−16
	$CHBr_3$	16.8	14.1	−9
61b	$CDCl_3$	13.9	7.5	−22
	CH_2Cl_2	14.1	6.8	−24
61c	$CDCl_3$	—	—	−11
61d	$CDCl_3$	15.3	14.1	−4

[a] In cal mol^{-1} K^{-1}.

The lowest barrier was found for hexacoordinate silicon dichlorides, while the barriers for analogous germanium and tin derivatives almost do not differ. As in complexes **56**–**58** (see Table 10), the barriers to enantiomerization do not depend on the solvent. No final conclusion in favour of a particular permutation mechanism was drawn: the authors cited [177–182] discussed all possible mechanisms including both non-dissociative and dissociative ones.

IV. Anionic complexes of tetravalent elements

1. Pentacoordinate chelate anions

The exchange between fluorine atoms in the axial and equatorial positions takes place in the TBP structures of most anionic silicon fluoride complexes, which became historically the first models for studying the permutation processes in the coordination unit of Group 14 elements.[183] The exchange rate increases with an increase in the number of fluorine atoms and upon the introduction of electron-withdrawing substituents into the phenyl group of aryl fluoride complexes and decreases under the action of bulky, sterically strained substituents at the silicon atom. Thus in solutions of complexes containing $[SiF_5]^-$ ions and acyclic $[RSiF_4]^-$ and $[R_2SiF_3]^-$ ions, the ^{19}F NMR spectra exhibit an averaged signal of fluorine atoms over the whole temperature range irrespective of the medium polarity due to their fast position exchange.[183,184] An exception is $[K(18\text{-crown-6})]^+[2,4,6\text{-}Bu^t_3C_6H_2SiF_4]^-$, as the exchange in its anion has a rather large activation energy (12.8 kcal mol^{-1}).[185] This is due to steric restrictions caused by the presence of two bulky *ortho*-substituents in the phenyl group.[185]

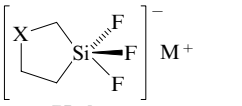
In acyclic anions $[R_2SiF_3]^-$ (**61**–**74**), the activation free energies of permutational isomerization vary in the range of 9–13 kcal mol^{-1} (see [183–186]).

Anion	$\Delta G^{\#}$ (see [a])	Anion	$\Delta G^{\#}$ (see [a])
$[(4\text{-}NO_2C_6H_4)_2SiF_3]^-$ (**61**)	8.8	$[(4\text{-}MeC_6H_4)_2SiF_3]^-$ (**69**)	10.7
$[(1\text{-Naph})_2SiF_3]^-$ (**62**)	9.3	$[(4\text{-}MeOC_6H_4)(Ph).SiF_3]^-$ (**70**)	10.8
$[(4\text{-}CF_3C_6H_4)(Ph).SiF_3]^-$ (**63**)	9.7	$[2\text{-}MeC_6H_4.(2,6\text{-}Me_2C_6H_3)SiF_3]^-$ (**71**)	11.3
$[(2\text{-}MeC_6H_4)_2SiF_3]^-$ (**64**)	9.9	$[(2,6\text{-}Me_2C_6H_3)(Ph).SiF_3]^-$ (**72**)	11.4
$[(4\text{-}ClC_6H_4)(Ph).SiF_3]^-$ (**65**)	10.2	$[(2,6\text{-}Me_2C_6H_3).(3,5\text{-}Me_2C_6H_3)SiF_3]^-$ (**73**)	12.3
$[Bu^t(Ph)SiF_3]^-$ (**66**)	10.4	$[(2,6\text{-}Me_2C_6H_3)_2SiF_3]^-$ (**74**)	13–14
$[Ph_2SiF_3]^-$ (**67**)	10.4		
$[PhMeSiF_3]^-$ (**68**)	10.7		

[a] In kcal mol^{-1}.

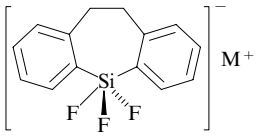
In the anions with *para*-substituted phenyl groups, electron-withdrawing substituents (anions **61**, **63**, **65**) decrease the barrier to permutational isomerization, while electron-donating substituents (anions **71**, **72**) increase this barrier. However, in difluoride $[Ph_3SiF_2]^-$ no fluorine exchange takes place even at elevated temperatures,[186] which is apparently due to the high configurational stability of complexes with apical fluorine atoms and the necessity of replacement of the axial fluorine atom by a Ph group during the exchange.

In silacycloalkanes with six- (**75b**)[187] and seven-membered rings (**76**),[188] the barriers to permutational isomerization (9.1 and 10.5 kcal mol^{-1}, respectively) are comparable with the barriers calculated for acyclic anions $[R_2SiF_3]^-$ (**61**–**74**). The lowest barrier is typical of the anions with five-membered silacarbocycles (**75a** [187] and **77** [189]). The pseudorotation in these compounds is so fast that the ^{19}F NMR spectra show only the averaged signal of axial and equatorial fluorine atoms even at low temperatures (−105 °C). The activation barrier for anion **77** estimated from the Eyring equation (1) is < 6 kcal mol^{-1} (Ref 189).



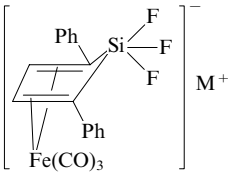
75a,**b**

X = $(CH_2)_n$ (n = 1 (**a**), 2 (**b**));
M = [K(18-crown-6)].



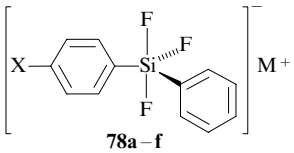
76

M = [K(18-crown-6)].



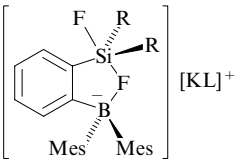
77

M = [K(18-crown-6)].



78a–**f**

X = CF_3 (**a**), Cl (**b**), H (**c**), Me (**d**), OMe (**e**), NMe_2 (**f**);
M = [K(18-crown-6)].



79a–**d**

R = Ph: L = [2.2.2]cryptand (**a**), 18-crown-6 (**b**);
R = Me: L = [2.2.2]cryptand (**c**), 18-crown-6 (**d**).

For anions **78a**–**f**, a linear correlation between the activation barrier to permutation and the Hammett constants (σ_p^+) was found.[190] As can be seen from the data presented below, the growth of electron-withdrawing properties of substituents results in lower $\Delta G^{\#}$ value.

Anion	$\Delta G^{\#}$ /kcal mol^{-1}	Anion	$\Delta G^{\#}$ /kcal mol^{-1}
78a	9.7	**78d**	10.8
78b	10.2	**78e**	11.6
78c	10.4	**78f**	12.3

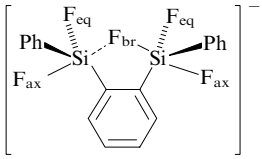
The temperature dependence of the ^{19}F NMR signals of complexes **79a**,**b** attests to exchange involving two fluorine atoms.[191] The activation barrier of the process calculated at the coalescence temperature (88 °C) was 15 kcal mol^{-1}. However, in the spectra of complexes **79c**,**d**, no coalescence was observed (up to 110 °C).

The conclusion about the intramolecular character of ligand exchange in pentacoordinate anionic silicon fluoride complexes was based on the retention of the $^{29}Si-^{19}F$ coupling constants in the ^{29}Si and ^{19}F NMR spectra over the whole temperature range of measurements (from +30 to ~ −100 °C).[5,185,187,192] It was shown that for mixed systems $SiF_4-[SiF_5]^-$, $MeSiF_3-[MeSiF_4]^-$, $PhSiF_3-[PhSiF_4]^-$, $SiF_5^--[SiF_6]^{2-}$, $MeSiF_3-[SiF_6]^{2-}$, additives (HF, MeOH, H_2O, F^-, pyridine, $[Pr^n_4N]^+[MeSiF_4]^-$) can both catalyze and inhibit the intermolecular exchange.[193,194]

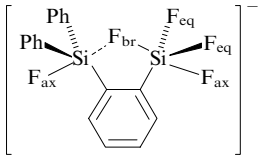
As a result of fast dynamic equilibrium, the NMR spectra of most anionic pentacoordinate acyclic alkoxysilanes exhibit only broadened signals of the indicator groups. Exceptions are the ions $[(Pr^iO)_3SiH_2]^-$ (**80**) and $[(Bu^tO)_3SiH_2]^-$ (**81**) where the ^1H NMR signals of the two protons are separate singlets at room temperature. The measured $\Delta G^{\#}$ value for ion **80** in deuteriotoluene was 16.3 kcal mol^{-1} (Ref. 195).

Quantum chemical calculations result most often in lower barriers to pseudorotation compared to experimental values obtained by DNMR. Thus according to semiempirical (AM1) and *ab initio* [MP2/6-31++G(d,p)] calculations, the barriers of this process in $[SiH_5]^-$ and $[SiH_4F]^-$ are only 2.4 and 2.3 kcal mol^{-1}, respectively.[196,197] Similar $\Delta G^{\#}$ values were found for $[SiF_5]^-$ and $[SiCl_5]^-$ (~3 kcal mol^{-1}).[198] In the authors' opinion, this is due to the fact that the potential energy surface tends to SP with an increase in the number of electronegative substituents at silicon. The permutation barriers for heavier Group 14 homologues are close to that calculated for the $[SiH_5]^-$ anion: 2.4 kcal mol^{-1} for $[GeH_5]^-$ and 1.7 kcal mol^{-1} for $[SnH_5]^-$ (Ref. 197). According to quantum chemical calculations, the mechanism of permutational isomerization in the $[FSiH_4]^-$, $[F_2SiH_3]^-$ and $[F_3SiH_2]^-$ anions includes the attack on the silicon atom by fluoride or hydride ions to give hexacoordinate intermediates.[48,199]

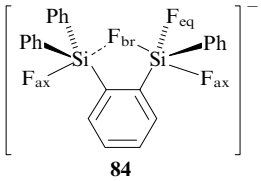
For the permutational isomerization of monodentate ligands in the coordination units of anions **82**–**84**,



82

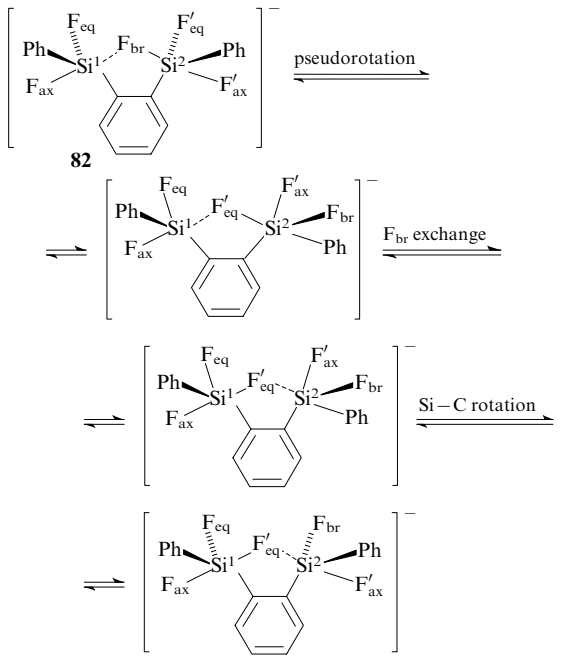


83



84

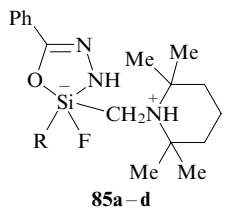
resulting in averaging of the ^{19}F NMR signals of all fluorine atoms, a mechanism including pseudorotation, exchange involving the bridging fluorine atom and rotation around the Si–C bond was proposed.[200]



82

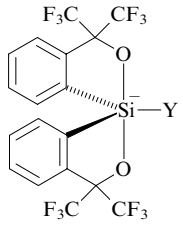
In these complexes, the exchange involving the bridging fluorine atom $F_{br}-Si^1 \rightleftarrows F_{br}-Si^2$ is fast on the NMR time scale: even at −90 °C, the signals of two silicon atoms in the ^{29}Si NMR spectrum are indistinguishable.

In chiral monochelate complexes **85a–d**, two stereodynamic processes take place, namely, silicon and nitrogen inversions. The activation energies found by DNMR are as follows: 20.7 (compound **85c**) and 11.7 kcal mol^{-1} (**85d**) for the former process and 17.0 (**85a–c**) and 20.8 kcal mol^{-1} (**85d**) for the latter process.[201]



85a–d

R = Me (**a**), Pr^i (**b**), Bu^t (**c**), F (**d**).



86a–j

Y = Bu^n (**a**), 4-MeOC$_6$H$_4$ (**b**), Ph (**c**), 3,5-(CF$_3$)$_2$C$_6$H$_3$ (**d**), OPh (**e**), CN (**f**), PhMeCH (**g**), F (**h**), C$_6$F$_5$ (**i**), 3-CF$_3$C$_6$H$_4$ (**j**).

The barrier to permutational isomerization for anions **86a–j** does not depend on the concentration or solvent polarity (1,2,4-trichlorobenzene–$C_6D_5NO_2$ mixture, 1,2-dichloroethane or CD_3CN).[202, 203] The $\Delta G^{\#}$ value for anion **86c** is lower (Table 13) than that for isostructural isoelectronic phosphorane ($\Delta G^{\#}$ = 28.3 kcal mol^{-1}).[204, 205]

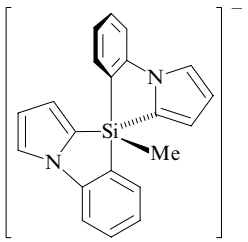
The lack of dependence of the exchange rate in anions **86a–j** on the addition of external nucleophiles (hexamethylphosphoric triamide and hexamethyldisilazane) and relatively low activation entropy (see notes to Table 13) rule out the associative mechanism, resulting in the formation of hexacoordinate transition state or intermediate.[202, 203] In view of high inversion barriers, irregular mechanism of the process *via* Si–O bond cleavage is unlikely.

Table 13. Activation free energies of silicon inversion in anions **86** (in $C_6D_5NO_2$).[202]

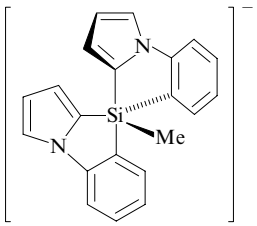
Anion	Cation	$\Delta G^{\#}_{424}$ /kcal mol^{-1}
86a	Et_4N^+	28.6
86b	Et_4N^+	26.6 [a]
86c	Et_4N^+	26.0
86d	$Bu^n_4N^+$	25.5
86e	Li^+	20.4
86f	$(Me_2N)_3S^+$	16.8
86g	Me_4N^+	29.0
86h	$(Me_2N)_3S^+$	17.5 [b]
86i	$Bu^n_4N^+$	21.9 [c]
86j	Et_4N^+	25.6

[a] In this case, $\Delta G^{\#}_{430}$. [b] According to other data:[203] $\Delta G^{\#}$ = 16.6 kcal mol^{-1}, $\Delta H^{\#}$ = 14.1 kcal mol^{-1}, $\Delta S^{\#}$ = −8 cal mol^{-1} K^{-1}. [c] $\Delta H^{\#}$ = 23.8 kcal mol^{-1}, $\Delta S^{\#}$ = 4.5 cal mol^{-1} K^{-1}.

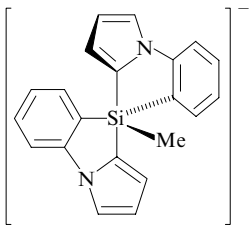
According to B3LYP/6-31G(d) calculations, pentacoordinate anion **87** has three stable diastereomers (**87**, **87′** and **87″**) with different orientations of two identical bidentate ligands.[206]



87



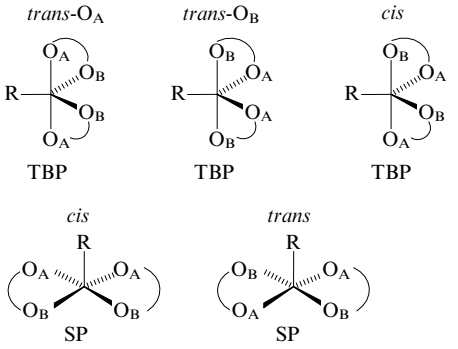
87′



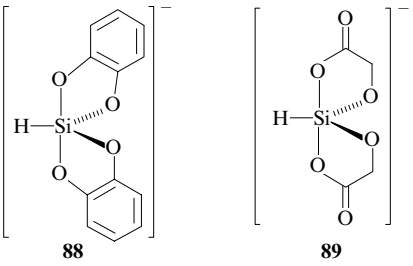
87″

In the NMR spectra of this anion the authors found only two sets of signals: the signals with higher intensity were assigned to diastereomer **87**, whereas for the minor set of signals it was impossible to distinguish between diastereomers **87′** and **87″**.[206] Interconversions involving these diastereomers can occur through Berry pseudorotation or turnstile rotation. ^1H DNMR data indicate that diastereomer **87** is thermodynamically more stable (by ~1.7 kcal mol^{-1}) than diastereomers **87′** and **87″** and the barrier to the **87** ⇄ **87′**(**87″**) transition is 15.5 kcal mol^{-1}. This is consistent with quantum chemical data (1.8 and 15.0 kcal mol^{-1} for these values, respectively).[206]

The anionic complexes of pentacoordinate silicon, germanium and tin with two identical unsymmetrical O,O-bidentate ligands can *a priori* exist as five different geometric isomers with different TBP and SP configurations.[207–210]

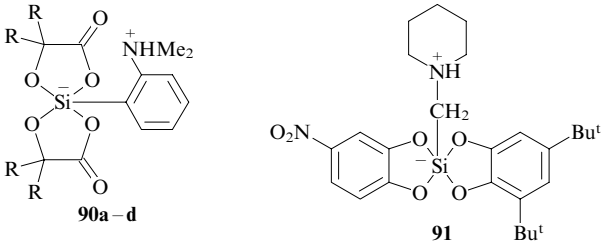


Quantum chemical (*ab initio* SCF-MO) calculations of anion **88** have shown that its ground state has a nearly TBP geometry.[208] Similar results were obtained [208] during quantum chemical analysis of anion **89**.[209]



In the case of these anions, Berry pseudorotation with a hydrogen atom as the reference ligand resulting in TBP diastereomer has a very low activation barrier (1.39 kcal mol^{-1}). Conversely, two successive Berry pseudorotations with oxygen as the reference atom have much higher activation energy (15.9 kcal mol^{-1}). The latter mechanism is supported by similarity of the $\Delta G^{\#}$ values determined by DNMR (16.6 kcal mol^{-1}) and calculated theoretically.[210, 211]

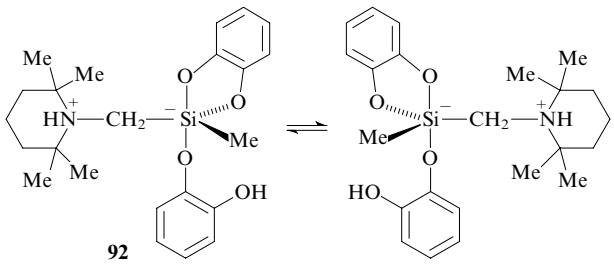
A rather high barrier to ligand permutation (20.7 kcal mol^{-1}) is also characteristic of complexes with bulky *tert*-butyl substituent (**90a**).[212] Since the geometry of this complex resembles a square pyramid, Berry pseudorotation was proposed as the process mechanism. The replacement of the *tert*-butyl group by F atom (**90b**) results in a decrease in $\Delta G^{\#}$ to 11.7 kcal mol^{-1} (Ref. 212).



R = Bu^t (**a**), F (**b**), H (**c**), Me (**d**).

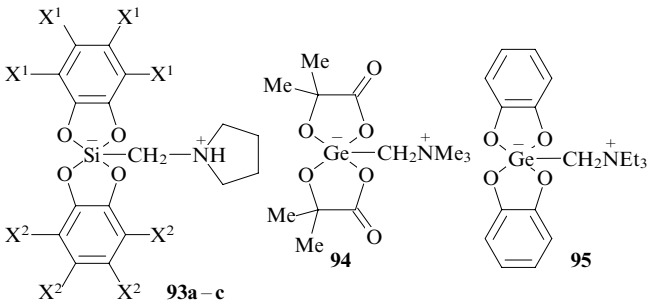
The NMR spectra of complex **91** contain signals of two TBP diastereomers assigned to *trans*-O- and *cis*-O-structures.[213] The calculated activation barriers were 16.7 and 17.2 kcal mol^{-1} , respectively.

Compound **92**, which is configurationally stable on the NMR time scale at room temperature, was found to undergo enantiomerization at silicon.[208] The $\Delta G^{\#}$ value calculated at the coalescence temperature (T_c = 65 °C) of the ^{1}H NMR signals of the $SiCH_2N$ group was 16.3 kcal mol^{-1} (Ref. 208).



In equimolar mixture of compounds **90c** and **90d** in DMSO-d_6, intermolecular ligand exchange similar to process (7) takes place.[212] This gives a zwitter-ion with different bidentate ligands; its chemical shift $\delta(^{29}Si)$ is equal to the arithmetic mean between the $\delta(^{29}Si)$ values of compounds **90c** and **90d**.

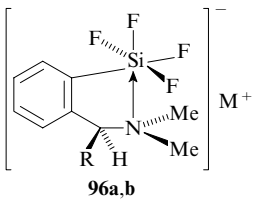
The exchange process for complexes **93a**,**b** results in zwitter-ion **93c**.[211] Germanium analogues of the silicon anions, for example, zwitter-ions **94** and **95**, have much higher stereochemical stabilities, and no stereodynamic processes were found for these compounds in solutions.[200, 211]



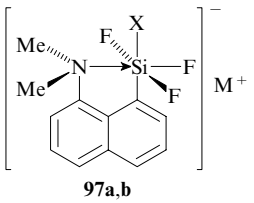
X^1 = X^2 = Cl (**a**), Br (**b**);
X^1 = Cl, X^2 = Br (**c**).

2. Chelate hexacoordinate anions with the N → Si and O → Si bond

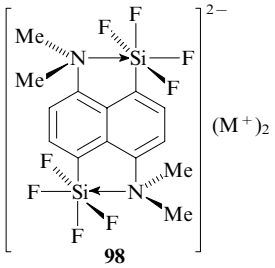
Publised data on the stereodynamic behaviour in solution of anions with hexacoordinate silicon atom known to date are limited to complexes **96**–**99** {M$^+$ = [K(18-crown-6)]$^+$} in which position exchange of fluorine atoms fast on the NMR scale takes place at room temperature.[128, 214]

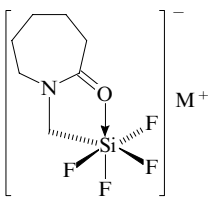


R = H (**a**), Me (**b**).



X = F (**a**), Ph (**b**).



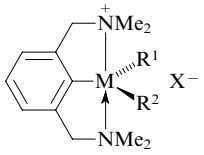


For this process, Bailar and Ray–Dutt mechanisms have been considered.[128,214] The calculated $\Delta G^{\#}$ values for complexes **96** and **97** vary in the range from 11 to 15 kcal·mol^{-1}. Using anions **97** as examples, it was found that the nature of substituent X does not affect the activation barrier to permutational isomerization.[214]

V. Cationic complexes of tetravalent elements

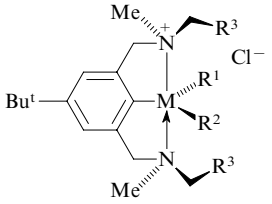
1. Complexes with N → M coordination bond (M = Si, Ge, Sn)

The trigonal-bipyramidal structure both in solution and in the solid phase is typical of cationic complexes **100**,[147,215–217] **101**,[218] **102**, **103** [219] with so-called pincer tridentate N,C,N-chelating ligands.



100, **101**

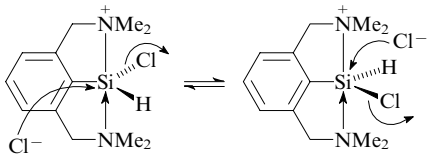
100: M = Si: X = Cl, Br, I, OTf, $[3,5\text{-}(CF_3)_2C_6H_3]_4B$, Ph_4B, BF_4; R^1, R^2 = H, Me, Ph, $PhCH_2$, $CH_2{=}CH$, Cl;
101: M = Sn: X = Br;
R^1, R^2 = Me, Et, Ph.



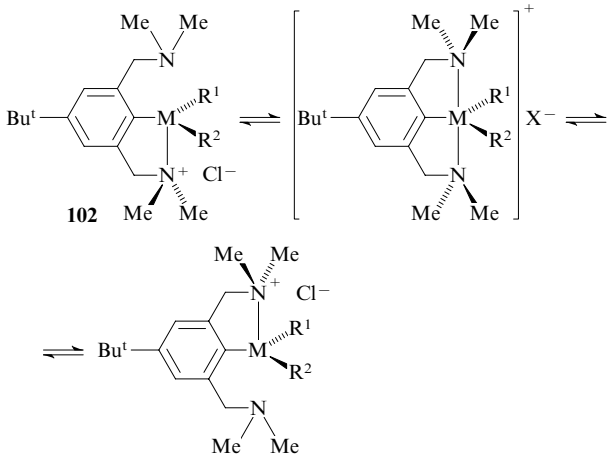
102a,**b**; **103a**–**c**

102: M = Si, R^3 = H:
$R^1 = R^2$ = Me (**a**); R^1 = Me, $R^2 = CH_2{=}CH$ (**b**);
103: M = Ge: R^3 = H:
$R^1 = R^2$ = Me (**a**),
4-Bu^t-3-MeC_6H_3 (**b**);
$R^1 = R^2 = R^3$ = Me (**c**).

The structure of complexes **100** is determined by the nature of the anion: for example, relatively nucleophilic anions (Cl^-, I^-) stabilize the tetracoordinate state of silicon, less nucleophilic tetraarylborate anion, pentacoordinate state, and tetraphenylborate anion, both states.[147,217] In solutions such complexes undergo ligand permutation with configuration inversion at the central atom as a result of attack of silicon by the halide ion.[147,217]



Complexes **100**–**102** occur in dynamic equilibrium fast on the NMR time scale similar to that found for neutral complexes of pentacoordinate silicon (compound **19b**), for example:[218,219]



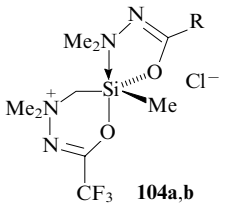
102

A similar scheme was also proposed for the complexes R_2[NCN]SnOAc (R = Ph, Bu, Me).[220] Going from silicon derivatives to their Ge analogues (complexes **103a**,**b**) is accompanied by an increase in $\Delta G^{\#}$ (Table 14). A similar change in the activation barrier was found for neutral complexes of pentacoordinate silicon with the O → M bond (see Section II.3).

Table 14. Activation parameters of dissociation of the N → Ge ICB in complexes **103**.[219]

Compound	Solvent	$\Delta G^{\#}$/kcal mol^{-1}	T_c/°C
103a	CD_3OD	9.5	−70
	C_2D_5OD	9.8	−63
103b	CD_3OD	14.1	15

The activation barriers determined by ^{1}H DNMR for fast, on the NMR time scale, configuration inversion of the chiral silicon atom in pentacoordinate complexes **104a**,**b** with different bidentate ligands were 17.2 and 16.9 kcal mol^{-1}, respectively.[221]

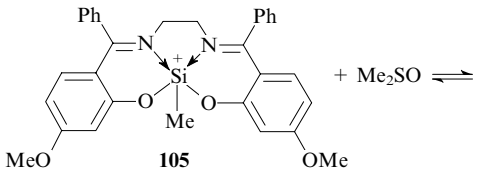


104a,**b**

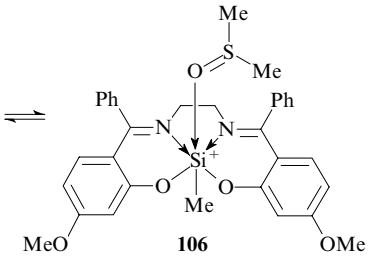
R = Bu^t (**a**), Ph (**b**).

These results, however, do not allow one to distinguish between two possible mechanisms of silicon inversion: intramolecular non-dissociative exchange and reversible dissociation of the N → Si bond.[221]

Solvation of cation **105** in DMSO is an exothermic process ($\Delta H = -5.2$ kcal mol^{-1}).[222] The hexacoordinate state of Si atom in complex **106** is indicated by an upfield shift of the ^{29}Si NMR signal (−159.3 ppm). An increase in temperature results in dissociation of complex **106** ($\Delta S = -20.4$ cal mol^{-1} K^{-1}).[223]



105



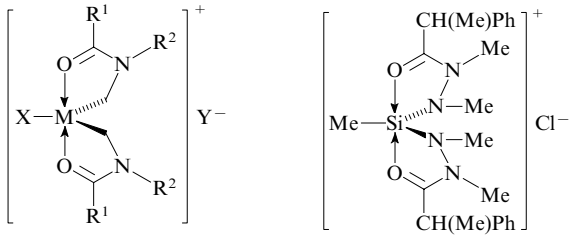
106

2. Complexes with O → M coordination bond (M = Si, Ge)

a. Mononuclear complexes

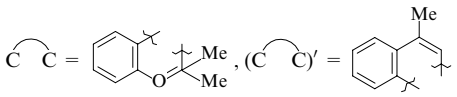
Complexes **107**–**109** [223–230] and **110** [231] with two monodentate substituents considerably differing in the nucleofugal properties have a nearly ionic structure. A

stereodynamic process, slow on the NMR time scale, resulting in averaging of diastereotopic protons of the NCH_2 group, takes place in the coordination TBP unit of these complexes. The $\Delta G^{\#}$ values are higher: more than 22–25 kcal mol^{-1} (for compounds **107**–**109**)[117] and 20.5 kcal mol^{-1} (**110**).[231]



107a–e; **108**; **109a,b** **110**

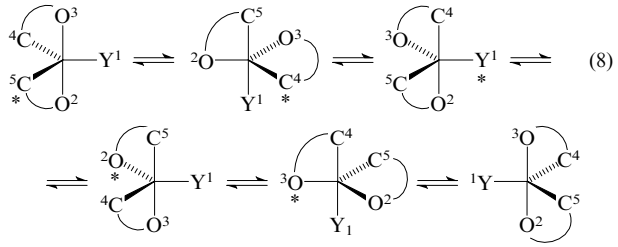
107: M = Si: X = F, Y = BF_4: $R^1 = R^2$ = Me (**a**), $R^1-R^2 = (CH_2)_3$ (**b**), C C (**c**), (C C)′ (**d**); X = F, Y = OTf, R^1-R^2 = C C (**e**);



108: M = Ge, X = Cl; Y = OTf, $OClO_3$, I, I_3;
$R^1-R^2 = (CH_2)_n$ (n = 3–5).

109: M = Ge, X = Br, $R^1-R^2 = (CH_2)_3$: Y = I (**a**), OTf (**b**).

The dissociation scheme with the formation of contact ion pairs $[L_2GeX]^+Y^-$ was proposed for complexes **108** on the basis of dependence of the electrical conductivity of their solutions on concentration (in the range of 0.5–11 mmol litre^{-1}).[11,117,232–234] The presented mechanism (8) of permutational isomerization includes dissociation of the M–Y bond in the first step (not shown) and subsequent five-step pseudorotation in the pentacoordinate cation (the reference atom is asterisked).[117]



(8)

Quantum chemical (DFT, PBE) calculations carried out according to this scheme demonstrate good agreement of experimental and theoretical (25 kcal mol^{-1}) $\Delta G^{\#}$ values.[117]

In cationic germanium bromide complexes **109**, permutation has a much lower barrier (7–9 kcal mol^{-1}, Table 15) than that in the fluorides or chlorides.

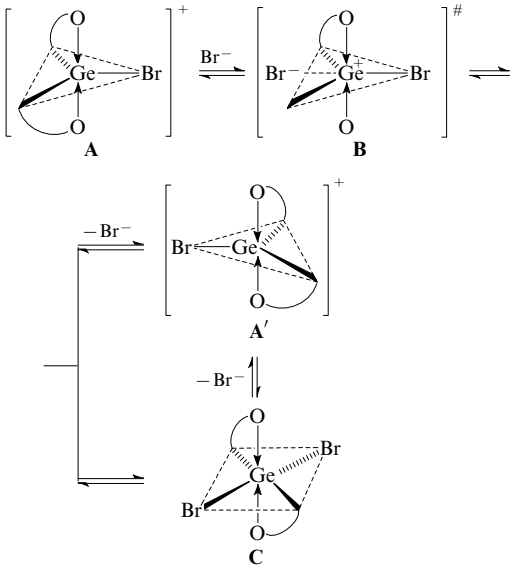
Table 15. Activation parameters of ligand exchange in complexes **109a,b**.[117]

Compound	Solvent	$\Delta G^{\#}$ (see [a])	$\Delta H^{\#}$ (see [a])	$\Delta S^{\#}$ (see [b])	T_c/°C
109a	$CDCl_3 + CD_2Cl_2$ (see [c])	7.7	0.5	−24	−103
	$C_6D_5CD_3$ (see [d])	15.4	12.0	−8	40
109b	$CDCl_3 + CD_2Cl_2$ (see [c])	8.9	3.4	−18	−73

[a] In kcal mol^{-1}. [b] In cal mol^{-1} K^{-1} [c] Solution concentration ~0.1 mol litre^{-1}. [d] Solution concentration ~0.01 mol litre^{-1}.

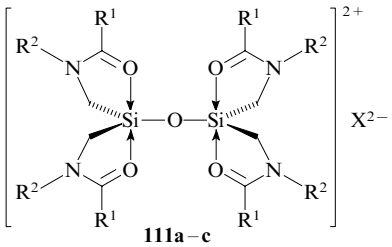
High nucleofugacity of monodentate ligands Br, I and OTf promotes ionization of the M–Y bond with subsequent dissociation in relatively polar solvents ($CDCl_3$, CD_2Cl_2) to give bischelate pentacoordinate cation **A** (Scheme 6). Then the Br^- anion attacks cation **A** from the rear with respect to Br atom; this results in configuration inversion at the central atom *via* transition state (**B**), *via* synchronous process **A** ⇄ **B** ⇄ **A**′, or upon the formation of *trans*-dibromide **C** (**A** ⇄ **B** ⇄ **C** ⇄ **A**′) as intermediate followed by elimination of Br^- anion.[117] This mechanism is supported by negative $\Delta S^{\#}$ value in equimolar mixture of $CDCl_3$ and CD_2Cl_2 (see Table 15) and high stability of *trans*-diastereomers of the dibromides of hexacoordinate germanium (see Section III.3.a).[117,169] An increase in the barrier to polytopic rearrangement by 7.7 kcal mol^{-1} in nonpolar $C_6D_5CD_3$ may be caused by the absence of dissociation of the bond with the monodentate ligand and a change in the ligand exchange mechanism (Section III.3.a).

Scheme 6



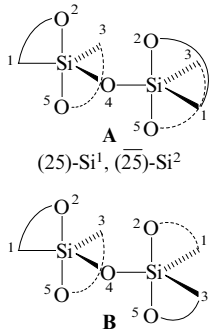
b. Binuclear complexes

The ^{1}H, ^{13}C and ^{29}Si NMR spectra of binuclear complexes **111** at room temperature were found to exhibit two sets of signals with different integral intensities assigned to two diastereomers (**A** and **B**).[235]



111a–c

$R^1-R^2 = (CH_2)_n$: n = 3, X = Hg_2Cl_6 (**a**); n = 4, X = $HgCl_4$ (**b**); n = 5, X = Hg_2Cl_6 (**c**).



A (25)-Si^1, ($\overline{25}$)-Si^2

B (25)-Si^1, (25)-Si^2

Only the signals of anisochronic protons of the prochiral NCH_2Si group, which are present in each set of signals as AB-system quartets, are well-resolved. The integral intensity ratio of the signals of two diastereomers depends on both the structure of the bidentate ligand and the nature of

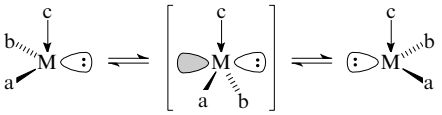
the solvent. For example, for complex **111b** the ratio changes from ~70 : 30 to ~60 : 40 on going from CD_2Cl_2 to DMSO.

An increase in temperature is accompanied by successive broadening and coalescence of the component of two proton doublets of the AB-system corresponding to the NCH_2Si group of complexes **111**. The $\Delta G^{\#}$ (T_c) values for compounds **111a–c** determined in DMSO at the coalescence temperature were 17.9 (78 °C), 18.5 (82 °C) and 16.4 (74 °C) kcal mol^{-1} (Ref. 235). For complex **111b** in less basic solvent (CD_2Cl_2), $\Delta G^{\#}$ is higher than 19 kcal mol^{-1}.

VI. Complexes of divalent elements

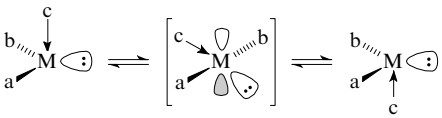
The pyramidal structure of the tricoordinate complexes of divalent Group 14 elements is related to the presence of stereochemically active lone pair. In these structures, intramolecular ligand exchange without bond cleavage proceeds through inversion for which two mechanisms have been proposed.

1. Vertex inversion is similar to the classical process in amines and occurs *via* planar trigonal transition state in which the lone pair is perpendicular to the plane of the molecule (D_{3h} symmetry).



Vertex inversion

2. Edge inversion is typical of tricoordinate compounds of Group 15 elements MX_3 (M = P, As, Sb)[236–240] and isoelectronic anions of divalent Group 14 elements $[M^{II}X_3]^-$ (M = Si, Ge, Sn, Pb). In this case, transition state is a planar T-shaped structure with planar arrangement of three ligands and the lone pair (C_{2v} symmetry).



Edge inversion

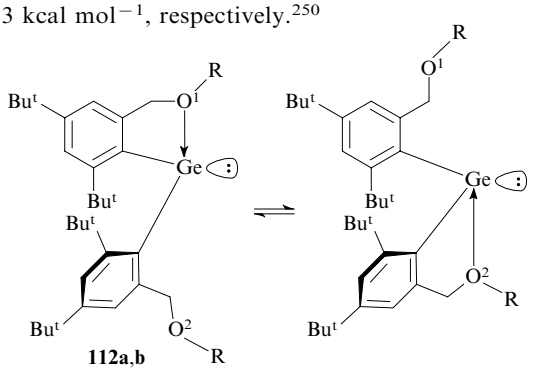
Theoretical (*ab initio*) calculations for the $[SiF_3]^-$, $[GeF_3]^-$, $[SnF_3]^-$, $[SnCl_3]^-$ and $[SnCl_2NH_2]^-$ anions attested in favour of the edge inversion mechanism. The barriers to the process are 40.3, 34.3, 27.8, 27.8 and 14.2 kcal mol^{-1}, respectively.[241]

1. Germylenes and stannylenes with the Z → M coordination bond (Z = N, O; M = Ge, Sn)

According to quantum chemical calculations (DFT) for the chelate $GeCl[PMe(C_6H_4CH_2NMe_2\text{-}2)]$, the inversion of the tricoordinate central atom rather than cleavage of the coordination bond is the optimal process resulting in a change in the Ge configuration.[242] The lower activation barrier for a T-shaped transition structure (38.5 kcal mol^{-1}) compared to the activation barrier for the trigonal planar state was attributed to the effect of the electron-withdrawing substituent. According to X-ray diffraction data, the germylene complex $Ge\{PMe(C_6H_4CH_2NMe_2\text{-}2)\}_2$ with two chelating ligands is tricoordinate. The calculated barrier to germanium inversion through the tetracoordinate pseudo-TBP intermediate is 3.0 kcal mol^{-1}, whereas the barrier to Ge inversion through the trigonal planar state is much higher (48.5 kcal mol^{-1}).[242] The fact that a trigonal rather than T-shaped transition state was identified is consistent with the replacement of Cl by less electronegative P in the coordination unit of the last-mentioned complex.

As in the case of molecular inversion, cleavage of the coordination bond of the central atom in tri- and tetracoordinate complexes results in a change of molecular configuration. In the NMR spectra of these complexes signal broadening is observed over the whole accessible temperature range. In some cases, the non-equivalence of atomic groups is also retained at high temperatures, for example, in tricoordinate chelates $GeR[C_6H_2CH_2NMe_2\text{-}2\text{-}Bu^t_2\text{-}4,6]$, where R = OEt, OPr^i, OBu^t, C≡CH, C≡CPh.[243] This points to fast dynamic processes for which the signal coalescence temperature could not be attained.[244–249]

The activation free energies for 'transcoordination' in $Ge(C_6H_2Bu^t_2\text{-}2,4\text{-}CH_2OR\text{-}6)_2$ (**112a**,**b**) determined at the coalescence temperature of the proton signals of the diastereotopic CH_2 groups are similar: 11.2 and 10.3 kcal mol^{-1}, respectively.[250]



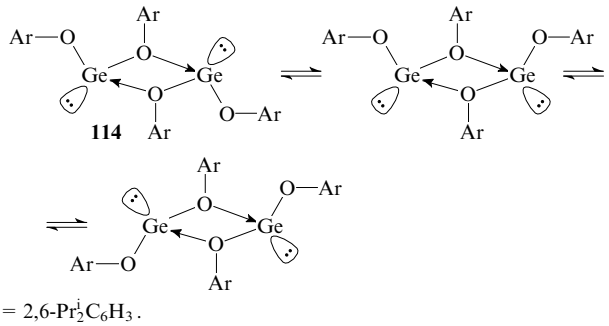
112a,**b**

R = Bu^t (**a**), Pr^i (**b**).

The 'transcoordination' activation barrier in the germylene $GeCl[OC_6H_2(CH_2NMe_2)_3\text{-}2,4,6]$ (**113**) has a similar value (10.7 kcal mol^{-1}).[251]

In the ^{1}H NMR spectrum of the germylene dimer $[Ge(OC_6H_3Pr^i_2\text{-}2,6)_2]_2$ (**114**) at room temperature, the proton signals of the Me groups of *ortho*-isopropyl substituents are manifested as a broadened doublet, which splits into two singlets as temperature decreases to −20 °C.[252] These signals were assigned to bridging and terminal groups. Splitting of one singlet into a doublet observed on further cooling of the solution to −60 °C is caused by the diastereotopic nature of the two bridging isopropyl substituents resulting from the transoid arrangement of the terminal aryloxy groups around the pyramidal Ge atoms.[252]

The first of the dynamic processes found for dimer **114** is accompanied by Ge inversion ($\Delta G^{\#} < 13.5$ kcal mol^{-1}),



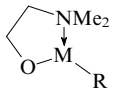
114

Ar = $2,6\text{-}Pr^i_2C_6H_3$.

resulting in the exchange by diastereotopic Me groups of the bridging aryloxy groups.[253]

The mechanism of the second dynamic process, exchange between the bridging and terminal positions of the aryloxy groups, remained obscure. The authors suggested either ring opening or dissociation of the molecule into monomers.[252]

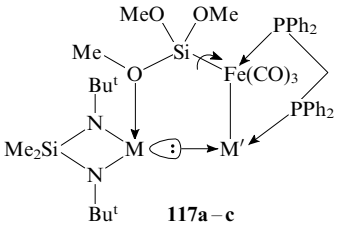
At low temperatures (about −80 °C), the ^{1}H NMR spectrum of complexes **115** and **116** consists of ABMX multiplets for the CH_2CH_2N protons and two signals of the diastereotopic methyl groups.[157] The observed spectral pattern corresponds to a structure with the N → Sn bond. On temperature rise, Me-group signals are broadened and then coalesce. The ABMX multiplets are thus converted into A_2X_2 multiplets.[157] The temperature variations in the NMR spectra indicate, in the authors' opinion, that reversible dissociation of the N → Sn bond takes place in these complexes. The activation energy determined by DNMR for complex **116c** was 10.2 kcal mol^{-1}, which is consistent with the data of quantum chemical calculations (DFT, 10.9 kcal mol^{-1}).[156]



M = Ge (**115**), Sn (**116**): R = $N(SiMe_3)_2$ (**a**), $O(CH_2)_2OEt$ (**b**), $O(CH_2)_2SMe$ (**c**).

115a–c, **116a–c**

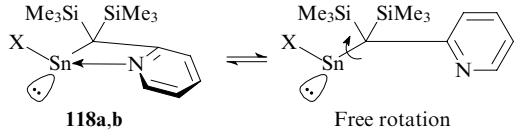
Unusual dynamic process takes place in transition metal complexes (**117**) in which the vacant p_z orbital as the acceptor and the occupied σ-orbital as the donor participate simultaneously in coordination interactions. The activation energies of the dynamic process resulting in the coalescence of ^{1}H NMR signals of the OMe groups were 15.5, 12.8 and 12.3 kcal mol^{-1} for complexes **117a–c**, respectively. It was suggested[253] that averaging of the OMe signals is due to cleavage of the O → M bond followed by rotation around the Si–Fe bond.



117a–c

M′ = Pd: M = Ge (**a**), Sn (**b**); M′ = Pt, M = Sn (**c**).

The activation barrier to the stereodynamic process resulting in averaging of the ^{1}H NMR signals of two $SiMe_3$ groups at the C atom of tricoordinate complex **118a** was 10.2 kcal mol^{-1} (Ref. 254). On the basis of downfield shift of the ^{119}Sn signal in $C_6D_5CD_3$ upon an increase in temperature from 5 °C (δ = 315.7 ppm) to 75 °C (δ = 329.4 ppm), the authors suggested that the process involves dissociation of the intramolecular coordination bond. For complex **118b** a similar exchange with close

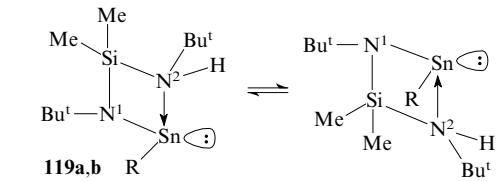


118a,b Free rotation

X = $N(SiMe_3)_2$ (**a**), Cl (**b**).

activation barrier $\Delta G^{\#}$ takes place (10.4 kcal mol^{-1}, T_c = −53 °C).[254, 255] Note that for complex **118a** hindered rotation of the $N(SiMe_3)_2$ group around the Sn–N bond also takes place ($\Delta G^{\#}$ = 18.2 kcal mol^{-1}).[254]

The dynamic process in complexes **119a,b** includes successive cleavage of the N^2 → Sn bond, inversion of the pyramidal N^2 atom, rotation around the N^1 → Sn bond and closure of the N^2 → Sn bond.[256, 257]

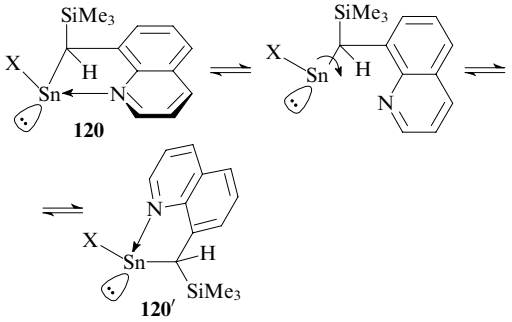


119a,b R = cyclo-C_5H_5 (**a**),  (**b**).

The $\Delta G^{\#}$ values for complexes **119a,b** (12.4 and 14.2 kcal mol^{-1}, respectively) were calculated at the coalescence temperature of the signals of non-equivalent $SiMe_2$ groups. The high barrier to intramolecular 'transcoordination' for indenyl derivative **119b** is consistent with stronger N^2 → Sn bond in the crystalline state (2.468 Å for **119a** and 2.312 Å for **119b**).[256] In complex **119b**, 1,3-migration of Sn between two carbon atoms of the indenyl group also takes place; the activation barrier for this process was estimated[256] as ∼14 kcal mol^{-1}.

The stannylenes considered above contain chelating ligands, which form four-membered rings in the presence of intramolecular coordination bond. The ligands discussed below form more stable five- or six-membered chelate rings.

The stereodynamic process resulting in coalescence of the ^{1}H NMR signals of the $SiMe_3$ group of complex **120** ($\Delta G^{\#}$ = 16.9 kcal mol^{-1}) was proposed to follow a mechanism involving two diastereomers (**120** and **120′**).[258]

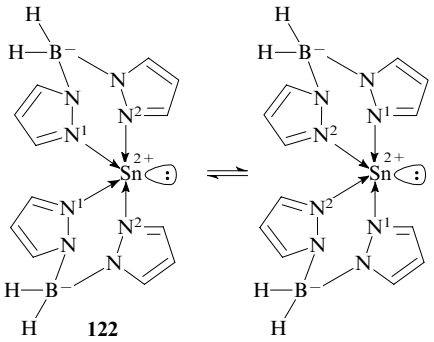


120 **120′**

Using DNMR in a PhMe + C_6D_6 mixture at a coalescence temperature, the activation barriers to the process resulting in coalescence of two signals of the $SiMe_3$ group in the complexes SnX[N(SiMe$_3$)CPhCHCPhN(SiMe$_3$)] with X = Cl and Br were found to be 16.6 and 17.4 kcal mol^{-1}, respectively.[259]

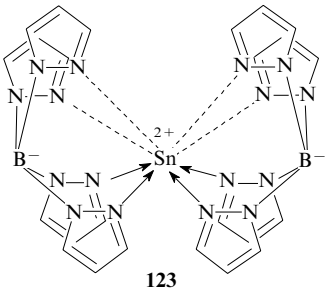
The activation energy for 'transcoordination' in $SnN(SiMe_3)_2[OC_6H_2(CH_2NMe_2)_3$-2,4,6] (**121**) is 16.4 kcal mol^{-1}, which is more than 5–6 kcal mol^{-1} higher than the barrier calculated for the tricoordinate germanium analogue **113**.[251] Note that the ^{1}H NMR spectrum of complex **121** exhibits at room temperature only two singlets of two *ortho*-NMe_2 groups.[251] The observed spectral pattern corresponds to a tetracoordinate tin atom.

The exchange barrier of the pyrazole rings in **122** was 10.2 kcal mol^{-1} according to ^{1}H NMR data.[260]



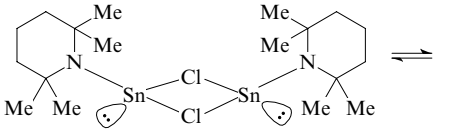
122

A study of the ^{1}H NMR spectra of the complex $[B(Pz)_4]_2Sn$ (**123**, Pz is pyrazol-1-yl) at various temperatures (from +24 to −87 °C) has shown[260] that only three pyrazole rings exchange positions in each of the $[B(Pz)_4]^-$ anions. The barrier to the process taking place through a pentacoordinate transition state is 10.5 kcal mol^{-1}.

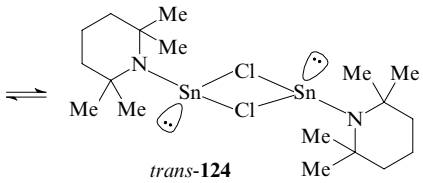


123

For distannylene **124**, which exists in the crystal as a dimer with bridging chlorine atoms and *cis*-arranged terminal substituents, *cis*–*trans*-isomerization was found in a $C_6D_5CD_3$ solution.[261]



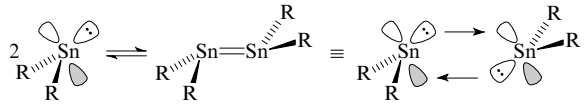
cis-**124**



trans-**124**

The activation parameters of this process calculated by full line shape analysis were as follows: $\Delta G^{\#} = 8.2$ kcal mol^{-1}, $\Delta H^{\#} = 70$ kcal mol^{-1} and $\Delta S^{\#} = 187$ cal mol^{-1} K^{-1}. The positive activation entropy implies that dissociation is the driving force of isomerization. As an alternative mechanism, the formation of ionic transition state $[R_2NSn]^+[Cl_2SnNR_2]^-$ was proposed.[261] Note that for complex $[Sn(\mu\text{-}Cl)N(SiMe_3)_2]_2$ with similar structure and *trans*-arranged terminal $N(SiMe_3)_2$ groups in the crystal, no *cis*–*trans*-isomerization was found.

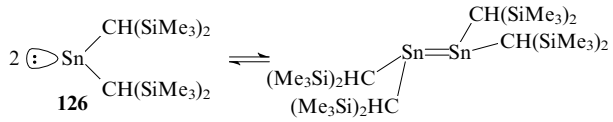
The isotropic ^{119}Sn NMR chemical shift (CP-MAS method) for the stannylene $Sn(C_6HBu^t\text{-}2\text{-}Me_3\text{-}4,5,6)_2$ (**125**) ($\delta_{iso} = 819$) attests to its dimeric structure in the crystalline state.[262] At low temperatures, fast equilibrium between the monomer and the dimer is established in $C_6D_5CD_3$; at 100 °C, it is shifted completely towards the monomer. The activation barrier calculated[263] at the coalescence temperature of ^{119}Sn NMR signals was 8.1 kcal mol^{-1}.



125

R = 2-Bu^t-4,5,6-Me_3C_6H.

The low-temperature (−108 °C) ^{119}Sn NMR spectrum (in toluene) of compound **126**, associated under these conditions into a dimer with Sn−Sn double bond,[264] exhibited two signals (740 and 725 ppm) close to the CP-MAS ^{119}Sn NMR signal (692 ppm).[265] On heating, a downfield shift and signal broadening took place, resulting in their disappearance at ∼−48 °C. At elevated temperatures, ^{119}Sn NMR spectra were found to exhibit a broad singlet at 2270–2315 ppm; as the temperature increased from 72 to 102 °C, the signal assigned to monomeric stannylene **126** underwent a slight downfield shift and narrowed down.

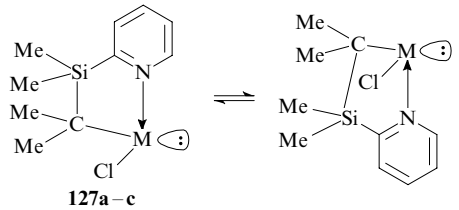


126

On the basis of temperature changes of the ^{13}C NMR signals of the methine carbon atom, the thermodynamic process parameters were estimated[265] to be $\Delta H = 12.8$ kcal mol^{-1} and $\Delta S = 7.9$ cal mol^{-1} K^{-1}. Note that spin − spin coupling constants $^1J(^{13}C-^{119}Sn)$ are the same for the monomer and the dimer, which is indicative of the retention of C−Sn bond order upon the formation of Sn−Sn multiple bond.

2. Plumbylenes with N → Pb coordination bond

The splitting of ^{1}H NMR signals (in THF-d_8) of plumbylene **127a** observed on decrease in temperature was attributed to an intramolecular process following a dissociative mechanism ($\Delta G^{\#} = 10$ kcal mol^{-1}, $T_c = -63$ °C).[101]



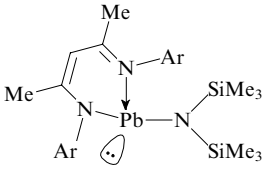
127a–**c**

M = Pb (**a**), Sn (**b**), Ge (**c**).

No signal coalescence was observed for isostructural Sn (**127b**) and Ge (**127c**) compounds. Signal broadening in the NMR spectra led to the conclusion that the strength of intramolecular coordination bond in solution increases in the series Pb < Sn < Ge. This is in line with the decrease in the bond length in the crystalline state: 2.466 Å (M = Pb), 2.271 Å (M = Sn) and 2.0814 Å (M = Ge).[101]

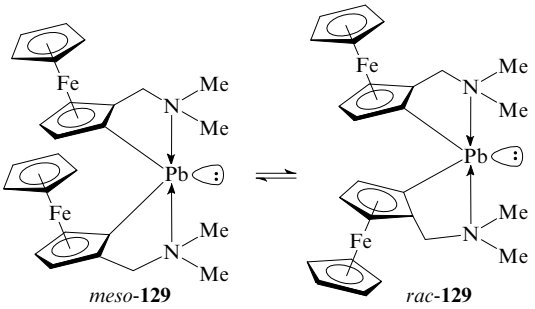
For hindered (by steric interactions of the bulky silyl and isopropyl groups) rotation around the Pb−$N(SiMe_3)_2$

bond in plumbylene β-diketiminate **128**, the $\Delta G^{\#}$ value at the coalescence temperature of $SiMe_3$ signals was calculated[266] to be 14 kcal mol^{-1}.



128 Ar = 2,6-$Pr^i_2C_6H_3$.

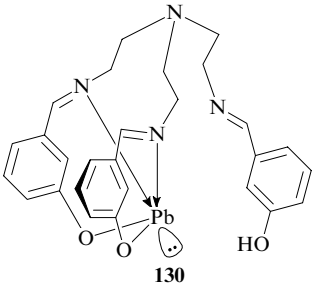
According to X-ray diffraction and ^{13}C NMR spectroscopy (CP-MAS), the plumbylene Pb{C,N-[Fe(η^5-C_5H_5)(η^5-$C_5H_3CH_2NMe_2$-2)]}$_2$ exists in the crystal as a chelate tetracoordinate *meso*-form.[267] Meanwhile in solution, both diastereomers, *meso*-**129** and *rac*-**129**, were identified by ^1H and ^{13}C NMR spectroscopy; their ratio varies from 6 : 1 to 8 : 1 depending on the solvent nature.



meso-**129** *rac*-**129**

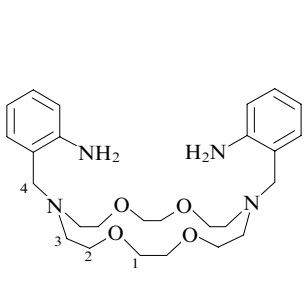
Averaging of the signals of non-equivalent ferrocenyl ligands in the *meso*-form is due to reversible dissociation of the N → Pb bond, fast on the NMR time scale.[267] On further cooling, intermolecular exchange between meso and racemic diastereomers was found to occur, which is an exceptionally rare case for plumbylenes. The thermodynamic parameters of this process are as follows: ΔH = 1.2 kcal mol^{-1}, ΔS = 0.24 cal mol^{-1} K^{-1}. Two possible exchange mechanisms were considered: synchronous intramolecular migration of two σ-bonded ferrocenyl groups and formation of the zwitter-ion structure with one ferrocenyl group followed by the shift of the second ferrocenyl group to the lead atom.[267]

At low temperature, the NMR spectra of complex **130** containing Schiff bases exhibited[268] two sets of signals of three ligands with integral intensity ratio of 2 : 1. An increase in temperature was accompanied by signal broadening. At the coalescence temperature of the azomethine proton signals, activation free energy of the process was determined (11.2 kcal mol^{-1}).

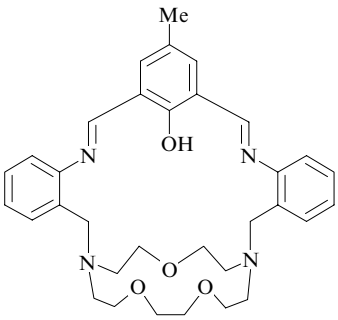


130

The ^1H NMR spectrum (in CD_3CN) of complex [PbL^1]·$(ClO_4)_2$ with C_{2h} molecular symmetry contained four signals due to aliphatic protons. At −5 °C, the geminal protons C^1H_2 are non-equivalent; however, as the temperature increases to 35 °C, their signals coalesce.[269] An opinion was stated that this was due to conformational exchange between the ligands in equatorial and axial positions of the five-membered chelate ring. The barrier to the process was 15.8 kcal mol^{-1}. The $\Delta G^{\#}$ value for a similar process in [PbL^1]·$(SCN)_2$ is lower (13.6 kcal mol^{-1}).[269]



L^1



L^2

The low-temperature (−25 °C) ^1H NMR spectrum (in CD_3CN) of the complex [PbL^2]·$(ClO_4)_2$ contained two singlets for imine protons, which are broadened and coalesce on heating to 47 °C.[269] Averaging of the signals at higher temperature is caused by dynamic exchange between the enantiomers where the Pb^{II} ion passes inside the macrobicyclic cage. The activation energy of the process calculated[269] at the coalescence temperature (T_c = 36 °C) of the aromatic proton signals of the phenolic fragment was 16.3 kcal mol^{-1}.

* * *

The presented published data on the stereochemical nonrigidity of a broad range of neutral, anionic and cationic complexes of di- and tetravalent Group 14 elements demonstrate convincingly that the use of multinuclear NMR spectroscopy and dynamic NMR spectroscopy for different nuclei in combination with other methods of physicochemical analysis considerably extended the views on the nature and mechanisms of stereodynamic processes. Of no little significance is also integrated analysis of the whole set of factors that affect the course and mechanism of stereodynamic processes: the nature of solvent, the structure of mono- and bidentate ligands, the presence of external nucleophile, *etc*.

Meanwhile, it should be borne in mind that the mechanisms discussed in the review are, to an extent, hypothetical and, therefore, they may be disputable. It is beyond doubt that further research in this, still intriguing, field of organoelement chemistry would not only provide answers to the existing questions but also bring about new, equally important problems.

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