# INFRARED STUDY OF INTRAMOLECULAR COORDINATION IN ORGANOGERMANIUM COMPOUNDS

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## Summary

Frequencies ($\nu$) and integrated intensities $A$ of Ge—H stretching modes in the IR-spectra of germanes, containing $GeCH_2Cl$ and $GeCHCl_2$, have been measured. The doublet character of the $\nu$(Ge—H) absorption bands has been explained by intramolecular coordination ($\alpha$-effect) between the chlorine and germanium atoms. The influence of solvents (heptane, carbon tetrachloride, tetrahydrofuran, acetone) on the shape of the $\nu$(Ge—H) absorption bands has been considered. The factors influencing the intensity of coordinated $\nu$(Ge—H) absorption bands have been analysed. The enthalpy of intramolecular coordination ($-\Delta H$) has been determined by spectroscopy. It has been shown that the $\alpha$-effect enthalpy increases with the increase of the acceptor properties of substituents bonded to the germanium atom.

## Introduction

Vacant $nd$ orbitals of the silicon subgroup elements (M) can participate in two types of electronic intramolecular interaction: (a) intramolecular $(p—d)\pi$ interaction in M—X fragments, where X is an atom with lone pair electrons or an $\alpha, \beta$-unsaturated hydrocarbon radical [1—3], (b) intramolecular coordination (IMC) or $(p—d)\sigma$ interaction between M and X atoms in compounds containing the $\geqslant M \xleftarrow{\underset{CH_2}{}} :X$ fragment [1,4—7].

Process (a) has been exhaustively studied and systematized for organometallic compounds of Group IVB [1,3,8]. Process (b) is currently under thorough investigation. However the experimental data obtained by physico-chemical methods are controversal. This is perhaps due to the low energy of the

M ← X bond formed [7]. Thus the influence of IMC on the spectroscopic para-
meters is small and it is often masked by other effects (i.e. solvation, conjuga-
tion, crystal effect etc.). Nonetheless IMC (along with other effects e.g. inductive
effect, $d_\pi$—$p_\pi$ interaction, $\sigma$, $\sigma$-; $\sigma$, $p$- and $\sigma$, $\pi$-conjugation) is one of the factors
resulting in the unusual properties of organometallic compounds containing
M—$CH_2$—X fragments ($\alpha$-effect). Atom X acts as a donor (using its lone pair
electrons) whereas the M atom behaves as an acceptor, using its $nd$-orbitals to
form a new weak M—X bond of $(p$—$d)\sigma$ type. Thus the experimental spectro-
scopic data show that for any $R_i$ and M in $(R_i)_3MCH_2Cl$ compounds (M = Si,
Ge, Sn) the electron density at the chlorine atom in the $CH_2Cl$ fragment is
always lower than that in the corresponding carbon analogs [4]. This is vividly
illustrated by spectroscopic study ($^1H$, $^{13}C$, $^{29}Si$ NMR and $^{35,37}Cl$ NQR) of
chloromethylsilane $H_3SiCH_2Cl$ and ethyl chloride $H_3CCH_2Cl$ [9]. The acceptor
properties exhibited by the silyl group due to the $\alpha$-effect result in a less polar
C—Cl bond in chloromethylsilane compared to that of ethyl chloride.

In general the influence of the $\alpha$-effect was not taken into account during inter-
pretation of the IR spectra of silicon subgroup compounds containing $CH_2X$
groups (X = Hal). There are, however, some exceptions [6,7]. Some anomalies
in the spectra are often explained by the existence of rotational isomers, of the
*trans* and *gauche* forms, of certain compounds [10—12]. However, although
the IR-spectral range below 1000 cm$^{-1}$ was used to indicate the presence of iso-
mers, the doublet character of $\nu$(M—H) bands was either not discussed or was
assigned to two types of stretching vibrations $\nu_s$(M—H) and $\nu_{as}$(M—H). The
$\alpha$-effect does not significantly influence the nature of the Si—H bond [13],
therefore the doublet character of the $\nu$(Si—H) band is mainly caused by con-
formational differences.

However, the experiment and the analysis of published data on the calcula-
tion of vibration spectra show [14] that the doublet character of $\nu$(M—H) bands
in the IR spectra of compounds containing the $MCH_2X$ fragment is caused by
intramolecular coordination of the type $\underset{\diagup}{\overset{\diagdown}{M}} \underset{CH_2}{\longleftarrow} :X$.

In fact the calculated values of $\nu_s$(M—H) and $\nu_{as}$(M—H) frequencies differ by
1—5 cm$^{-1}$ [10,12,15] and $\nu$(M—H) frequencies for *gauche* and *trans* conformers
differ by 1—3 cm$^{-1}$ [12,15]. At the same time the difference in $\nu$(M—H) frequ-
encies observed experimentally for compounds containing the $CH_2X$ fragment
is 20—35 cm$^{-1}$ [6,10,12,14].

Theoretical and experimental data obtained for ethylchlorosilanes [15] show
that the $\nu$(Si—H) band does not split into a doublet provided that molecules of
these compounds exist as two rotational isomers of *trans* and *gauche* forms.
Using $(R_i)_2HSiCH_2Cl$ compounds it was found [6,7] that the $\nu$(Si—H) absorp-
tion band consists of two bands which are best resolved in IR spectra of hep-
tane solutions. The low frequency band is assigned to the $\nu$(Si—H) vibration
in molecules participating in IMC ($\nu_c$), and the high frequency band is assigned
to vibrations in "free" molecules ($\nu_f$). The values of the $\nu_c$ frequency is in all
cases 20—25 cm$^{-1}$ smaller than that of the $\nu_f$ frequency. Comparison of inte-
grated intensity values of these bands show that $A_c$ is much higher than $A_f$. This
indicates the energy decrease and the rise of polarity of the Si—H bond in mole-
cules taking part in intramolecular coordination.

The analysis of $\nu$(Si—H) stretching mode frequencies and intensities show [6,7] that the degree of IMC in $(R_i)_2HSiCH_2Cl$ organosilicon compounds depends on: (1) the nature of $R_i$ substituents bonded to the silicon atom (steric factors, induction effects); (2) the nature of the solvent (electron-donating solvents may partially or totally destroy IMC).

It was believed that investigation of the integrated intensity of $\nu$(Ge—H) stretching modes in the IR spectra of germane derivatives containing chloromethyl groups would provide information on the principal characteristics of the $\alpha$-effect in organogermanium compounds. Therefore the aim of this investigation was to study the influence of IMC on both frequency and integrated intensity of $\nu$(Ge—H) stretching modes in the IR-spectra of $(R_i)_2HGeCH_2Cl$ compounds and to estimate the enthalpy of the above interaction. The published data on this problem were not known to the authors.

## Results and discussion

The values of measured frequencies and integrated intensities of Ge—H stretching modes of the compounds investigated are given in Table 1. This shows that the $\nu$(Ge—H) absorption band has a doublet character. As in the case of organosilicon compounds [6,7] it is caused by intramolecular coordination between the chlorine and germanium atoms realized through space ($\alpha$-effect). In our opinion the low frequency band may be assigned to the $\nu$(Ge—H) vibration in molecules with $\begin{subarray}{c}\text{Ge} \leftarrow :\text{Cl}\\ \text{CH}_2\end{subarray}$ intramolecular coordination. Indeed, we

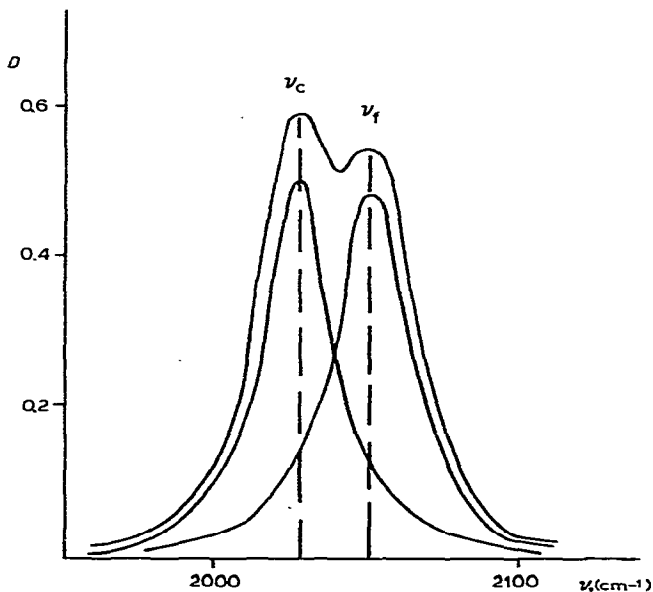have shown earlier that $\nu$(Ge—H) frequencies in the IR-spectra of $R_3$GeH deriv-



Fig. 1. Form of the absorption band of the $\nu$(Ge—H) stretching mode in the IR spectrum of diethyl(chloromethyl)germane (solvent, heptane).

TABLE 1

IR DATA

| No. | Compound | $\Sigma\sigma^*$ | $\nu(\text{Ge—H})(\text{cm}^{-1})$ | | $A^{1/2}(\times 10^2)$, $(\text{mol})^{-1/2}\,l\,\text{cm}^{-1}$ | | Composition (%) | | Enthalpy $(-\Delta H)$, $(\text{kJ mol}^{-1}) \pm 0.5$ |
|---|---|---|---|---|---|---|---|---|---|
| | | | $\nu_c$ | $\nu_f$ | $A_c^{1/2}$ | $A_f^{1/2}$ | $C_c$ | $C_f$ | |
| I | $(C_2H_5)_2HGe(CH_2Cl)$ | 0.85 | 2027 | 2051 | 1.67 | 1.13 | 25 | 75 | 2.1 |
| II | $(CH_3)_2HGe(CH_2Cl)$ | 1.05 | 2043 | 2064 | 1.62 | 1.09 | 30 | 70 | 3.3 |
| III | $CH_3(C_6H_5)HGe(CH_2Cl)$ | 1.65 | 2044 | 2066 | 1.38 | 1.30 | 40 | 60 | 4.2 |
| IV | $(C_2H_5)ClHGe(CH_2Cl)$ | 3.85 | 2077(sh) | 2098 | 1.26 | 1.17 | 35 | 65 | 4.6 |
| V | $(C_2H_5)_2HGe(CHCl_2)$ | 1.74 | 2046 | 2065(sh) | 1.53 | 0.91 | 40 | 60 | 5.0 |

atives are connected with the sum of inductive Taft constants for three R substituents by the linear relation

$$\nu(\text{Ge--H}) = 23.6 \, \Sigma\sigma^* + 2021 \qquad [16] \qquad\qquad (1)$$

The electron-donor properties of —$CH_2Cl$ and —$CHCl_2$ groups ($\alpha$-effect) are accompanied by a decrease of electron acceptor properties of these groups (I-effect). The latter results, in its turn, in a decrease in the Ge—H bond energy, force constant and stretching mode frequency $\nu(\text{Ge--H})$ of this bond. Therefore when germane derivatives exhibit an $\alpha$-effect, $\nu(\text{Ge--H})$ decreases in the IR spectra of coordinated molecules.

Let us consider the integrated intensity data ($A^{1/2}$). The integrated intensities of $\nu(\text{Ge--H})$ stretching modes for compounds I, II and V corresponding to the "free" form ($A_f^{1/2}$) were determined from the equation obtained previously

$$A_{\text{ind}}^{1/2} = 1.3 - 0.2 \, \Sigma\sigma^* (\text{heptane}) \qquad [16] \qquad\qquad (2)$$

For compounds III and IV, the substituents of which are capable of both inductive affect and $d_\pi$—$p_\pi$ interaction with germanium atom, $A_f^{1/2}$ was determined as a sum $A_{\text{ind}}^{1/2} + \Delta A^{1/2}$, where

$$\Delta A^{1/2} = 1.09 \, \Sigma\sigma_p + 0.36 \qquad [16] \qquad\qquad (3)$$

$A_f^{1/2}$ values obtained enable the determination of the concentration of "free" form ($C_f$) molecules. The concentration of molecules taking part in intermolecular coordination ($C_c$) was determined as a difference $C_{\text{total}} - C_f$, where $C_{\text{total}}$ is the initial concentration of germane derivatives. More details on the determination of $C_f$ and $C_c$ concentrations are given in the Experimental section. It follows from the Table that the integrated intensity of coordinated molecules ($A_c^{1/2}$) for germane derivatives containing alkyl substituents which exhibit exclusively +I- effect (compounds I, II and V) is approximately $0.55 \times 10^2$ mole$^{-1}$ l$^{1/2}$ cm$^{-1}$ higher than that of $A_f^{1/2}$. However upon introduction of electron acceptor substituents (compounds III and IV) capable of $d_\pi$—$p_\pi$ interaction (Ph, Cl) into the germane molecule the difference between $A_c^{1/2}$ and $A_f^{1/2}$ is only approximately $0.1 \times 10^2$ mole$^{-1}$ l$^{1/2}$ cm$^{-1}$. Let us consider the factors which may cause the difference between $A_c^{1/2}$ and $A_f^{1/2}$ values. On the one hand the decrease of the $A_c^{1/2}$ value might be due to weakening or distortion of the $d_\pi$—$p_\pi$ interaction in Ge—Cl and Ge—Ph fragments during intramolecular coordination. This in its turn might cause an increase in the acceptor properties of the above groups. It is seen from equation 2 that the values of integrated intensity decrease with the rise in the acceptor properties of substituents. Upon complex formation however (as shown for example for $SnCl_4$ and $SnBr_4$ complexes with different donors [17]) a notable increase in central atom positive change takes place. It is well known that the increase of central atom positive charge causes an increase, and not a decrease, in the degree $d_\pi$—$p_\pi$ interaction in Ge—Cl and Ge—Ph bonds [1,18,19].

On the other hand one might assume that the acceptor properties of the chlorine atom and phenyl group become higher upon complex formation in a manner analogous to the process taking place in acceptor complexes of $SnCl_4L_2$ and $SnBr_4L_2$ type [17]. In this case the electron density on the chlorine and bromine atoms considerably increases upon complex formation whereas electron density

on the central tin atom becomes less. Such redistribution of electron density is due to the change of central atom hybridization from $sp^3$ to $sp^3d$ during the formation of the complexes [17]. It is known for example [20] that when the hybridization of a carbon atom changes from $sp$ to $sp^2$ and $sp^3$ ($s$ character decrease) the electronegativity of this atom falls from 3.2 to 2.8 and 2.6, respectively. The germanium atom electronegativity alters upon the charge of hybridization from $sp^3$ to $sp^3d$ and becomes more electropositive. This leads in its turn to an increase of chlorine atom and phenyl group acceptor properties and to the decrease of integral intensity values of $\nu_c$(Ge—H) bands in compounds III and IV. Of the three substituents bonded to the germanium atom (apart from the chloromethyl group) in compounds I and II, the hydrogen atom shows the greatest acceptor properties. Therefore the shift of electron density from the germanium to the hydrogen atom takes place by intramolecular coordination between the chlorine and germanium atoms. This process is accompanied by a decrease of germanium atom electronegativity and by a rise in Ge—H bond polarity. Therefore $A_c^{1/2}$ values increase in compounds I and II and become much higher than the value of $A_f^{1/2}$. Peak intensities of $\nu$(Ge—H) bands corresponding to coordinated ($\nu_c$) and "free" ($\nu_f$) forms in the IR-spectra of compounds I—III in heptane solution are comparable and the bands are resolved relatively well. At the same time the $\nu_c$ band in the spectrum of compound IV is a low frequency shoulder of the $\nu_f$ band. For compound V the $\nu_f$ band is a high frequency shoulder of the $\nu_c$ band (Fig. 2). Since the amount of coordinated molecules in compound IV is half that of "free" molecules (see Table 1) the values of integrated intensity of coordinated ($A_c^{1/2}$) and non-coordinated ($A_f^{1/2}$) forms are close to each other; the $\nu_c$ absorption band corresponding to molecules participating in IMC shows as a shoulder in the IR spectrum. An approximately equal number of "free" and coordinated molecules is observed in compound V. However the much higher integrated intensity ($A_c^{1/2}$) results in a notably higher intensity of the band corresponding to coordinated molecules compared to the "free" molecule band intensity.

The ratio of coordinated and "free" molecules in the compounds investigated varies in time i.e. the number of coordinated molecules increases whereas the number of free molecules drops. This first and foremost indicated by a change in $\nu$(Ge—H) absorption band shape in the course of time: peak intensities of $\nu_c$ bands increased and those of $\nu_f$ bands become smaller. Repeated measurements and calculations carried out by the authors showed that the concentration of
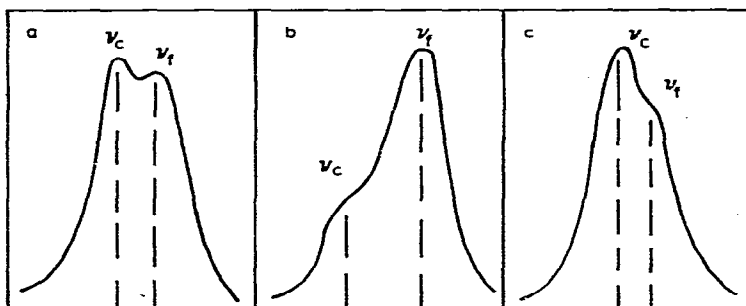


Fig. 2. Form of the absorption bands of the $\nu$(Ge—H) stretching mode in the IR-spectra of the compounds investigated (solvent, heptane). (a) compounds I—III, (b) compound IV, (c) compound V.

coordinated molecules increased by 5% in compounds I and II after a year and in compound III after six months (compounds IV and V have not been repeatedly studied). The dynamic equilibrium between "free" and coordinated forms is likely to be reached not at once but over a period of time. One of the reasons for this might arise from steric hindrance during coordination caused by the substituents at the germanium atom.

The IR spectra of compounds I—III recorded repeatedly after a year showed an absorption band of approximate frequency 385 cm$^{-1}$ corresponding to a $\nu$(Ge—Cl) stretching mode. This band is absent in freshly prepared compounds. Along with the abovementioned observation, approximately 7% of impurities are detected in compounds I—III by GLC. The appearance of a $\nu$(Ge—Cl) absorption band in the IR spectra suggests that the impurities are chlorogermanes of $R_2MeGeCl$ type.

Carbene decomposition of silicon and germanium analogs of hexahalogo-ethanes, accompanied by migration of one halogen atoms to the silicon or germanium atom was previously explained by $x_3M \overset{\longleftarrow}{\underset{MX_2}{\longrightarrow}} : x$ coordination (M = Si, Ge; $^1M$ = C, Ge) taking place in the transition state, using the $nd$-orbitals of the M atom and an electron pair from the X atom [21].

Taking this into consideration it is reasonable to assume that chlorogermanes are formed by the rearrangement $R_2 \; Ge \overset{H}{\underset{CH_2}{\longleftarrow}} :Cl \longrightarrow R_2GeCl \underset{CH_3}{} $ which slowly taken place on storage.

The influence of solvents (heptane, carbon tetrachloride, toluene, acetone) on the shape of the $\nu$(Ge—H) absorption band was studied, taking compounds I and III as an example. The concentration of coordinated molecules in heptane solutions of the above compounds amount to 25—40% and peak intensities of $\nu_c$ bands in the spectra are higher than those of $\nu_f$. The number of coordinated molecules notably decreases in electron-donating solvents. This is caused by competition of two processes: intramolecular coordination and solvation of the organogermanium compound with molecules of the electron-donating solvent at the germanium atom. Thus the ratio of coordinated and free molecules of compounds I—III in carbon tetrachloride solution changes such that the peak intensities of $\nu_f$ bands become higher than those of $\nu_c$ bands (Fig. 3). On consecutive addition of toluene or acetone to heptane solutions of the investigated compounds regular, a change of $\nu_c$ and $\nu_f$ bands peak intensity ratio takes place. The distortion of coordination in the molecules of compounds I—III is more rapid on addition of acetone than on addition of toluene. One broadened $\nu$(Ge—H) band is observed in the IR spectra of compounds I—III dissolved in pure toluene or acetone in contrast to the spectra of carbon tetrachloride solutions of these compounds. It seems that solvents of higher electron donor ability than carbon tetrachloride (i.e. toluene, acetone) completely destroy intramolecular coordination in these compounds.

The enthalpies of intramolecular coordination were estimated. It was determined that the value of IMC enthalpy depends on the nature of the substituents bonded to the germanium atom. The enthalpy of intramolecular coordination increases with the rise in acceptor properties of the substituents on transition from compound I to compound IV (Table 1). The contraction of the diffuse
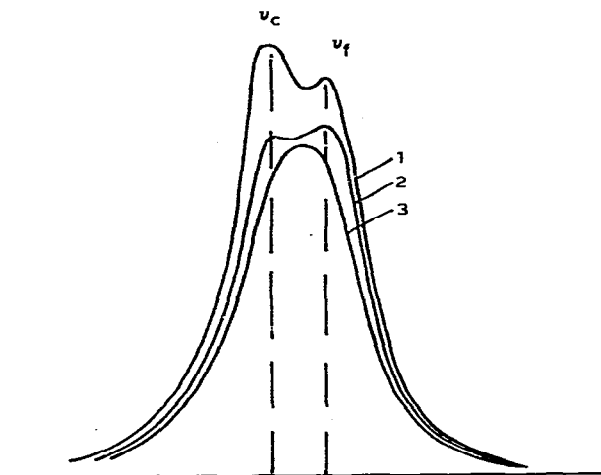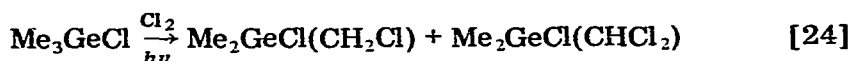
Fig. 3. Form of the absorption bands of the $\nu$(Ge—H) stretching mode in the IR spectra of compounds I—III. (1) in heptane solution; (2) in carbon tetrachloride solution; (3) in toluene (acetone) solution.

$nd$-orbitals of the germanium atom is likely to increase the overlap integrals of interacting $4d$ and $3p$ orbitals of the germanium and chlorine atoms on the introduction of an acceptor substituent into the molecule. In contrast to this, the experimental data for similar silane derivatives [22] indicate weakened intra-molecular coordination on the increase of substituents acceptor properties. Thus the contraction of the smaller $3d$ orbitals of the silicon atom results in the decrease of the overlap integrals of the silicon and chlorine atom interacting orbitals. These observations show that geometric parameters of $d$ orbitals play an important part in the formation of $(p\text{—}d)$ $\sigma$-type bonds.
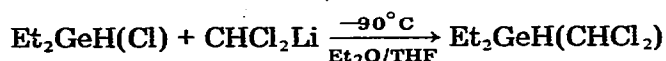
The number of chlorine atoms in the donor fragment of the molecule also significantly affects the IMC energy. The $\alpha$-effect for $R_3SiCH_{3-n}Cl_n$ compounds becomes smaller with increasing $n$, i.e. with the rise of substituents acceptor properties [23]. The reverse dependence is observed for germane derivatives (compounds I and V). In this case the rise of IMC energy in compound V (dichloromethyl derivative) is caused not only by the increase in the acceptor properties of the substituents bonded to the germanium atom. Thus the sum of the Taft inductive constants ($\Sigma\sigma^*$) of the three substituents for compounds III and V is practically the same, but $-\Delta H$ values are different. The increase of IMC enthalpy indicates the increased degree of overlap of interacting orbitals. Both chlorine atoms seem to participate in the formation of a dative $(p\text{—}d)$ $\sigma$-bond in diethyl(dichloromethyl)germane.

The compounds were prepared according to the following methods.
$Me_2GeH(CH_2Cl)$:

$$Me_3GeCl \xrightarrow[h\nu]{Cl_2} Me_2GeCl(CH_2Cl) + Me_2GeCl(CHCl_2) \qquad [24]$$

$$Me_2GeCl(CH_2Cl) \xrightarrow[Et_2O]{LiAlH_4} Me_2GeH(CH_2Cl)$$

Et$_2$GeH(CHCl$_2$):

$$\text{Et}_2\text{GeH(Cl)} + \text{CHCl}_2\text{Li} \xrightarrow[\text{Et}_2\text{O/THF}]{-90^\circ\text{C}} \text{Et}_2\text{GeH(CHCl}_2)$$
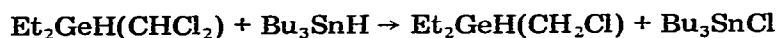
Dichloromethyllithium was prepared by the method of Kobrich [25]
Et$_2$GeH(CH$_2$Cl):

Et$_2$GeH(CHCl$_2$) + Bu$_3$SnH → Et$_2$GeH(CH$_2$Cl) + Bu$_3$SnCl

EtGeH(Cl)(CH$_2$Cl):

$$\text{EtGeCl}_3 + \text{CH}_2\text{N}_2 \xrightarrow[-60^\circ\text{C}]{\text{Et}_2\text{O . Cu}} \text{EtGeCl}_2(\text{CH}_2\text{Cl})$$

according to the method of Seyferth [26]

$$\text{EtGeCl}_2(\text{CH}_2\text{Cl}) \xrightarrow[\text{Et}_2\text{O}]{\text{LiAlH}_4} \text{EtGeH}_2(\text{CH}_2\text{Cl})$$

$$\text{EtGeH}_2(\text{CH}_2\text{Cl}) \xrightarrow{\text{ClCH}_2\text{OCH}_3} \text{EtGeH(Cl)(CH}_2\text{Cl})$$
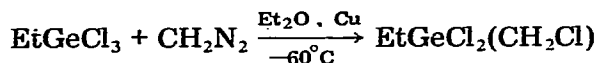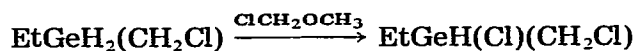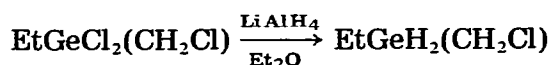
These partial chlorinations have been described [27].
PhMeGeH(CH$_2$Cl):

$$\text{PhMeGeH(Cl)} + \text{CHCl}_2\text{Li} \xrightarrow[-90^\circ\text{C}]{\text{Et}_2\text{O/THF}} \text{PhMeGeH(CHCl}_2) + \text{LiCl}$$

$$\text{PhMeGeH(CHCl}_2) + \text{Bu}_3\text{SnH} \xrightarrow{h\nu} \text{PhMeGeH(CH}_2\text{Cl}) + \text{Bu}_3\text{SnCl}$$
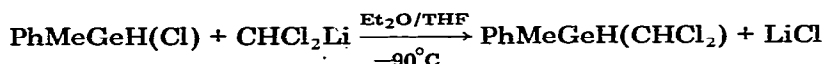
## Experimental

The compounds described in this paper were characterized using standard analytical technics GLC (Aerograph 90P, Varian 1200, SE 30) and NMR (Varian T60).

*Me$_2$GeH(CH$_2$Cl).*
The reduction of Me$_2$GeCl(CH$_2$Cl) (19 g, 0.110 mol) with LiAlH$_4$ in ether (2.09 g, 0.055 mol) leads, after hydrolysis and ether extraction to a solution which is dried over CaCl$_2$ and distilled: Me$_2$GeH(CH$_2$Cl), (13.50 g, 83% yield), B.p.: 99°C NMR (δ ppm): 4.18 (m, Ge—H), 2.96 (d, $J$(H—Ge—CH); 2.5 Hz, CH$_2$), 0.31 (d, CH$_3$).

*Et$_2$GeH(CHCl$_2$).*
Et$_2$GeHCl (16.71 g, 0.10 mol) is added dropwise at —90°C to CHCl$_2$Li (0.11 mol) (freshly prepared). The mixture is maintained at —90°C for 2 h and then warmed up to room temperature. After hydrolysis and pentane extraction, the solution obtained is dried over Na$_2$SO$_4$ and then distilled giving to Et$_2$GeH-(CHCl$_2$), (9.45 g, 44% yield). B.p.: 84°C/20 mmHg. NMR (δ, ppm): (CCl$_4$) 4.40 (m, Ge—H), 5.53 (d, $J$(H—Ge—CH) 2.5 Hz, CH), 1—1.40 (m, (C$_2$H$_5$).

*Et$_2$GeH(CH$_2$Cl).*
Bu$_3$SnH (6.33 g, 0.0217 mol) is added to Et$_2$GeH(CHCl$_2$) (4.7 g, 0.0217 mol).

An exothermic reaction takes place. The mixture is then refluxed for 1 h. Distillation in the presence of catalytic amounts of galvinoxyl and hydroquinone leads to $Et_2GeH(CH_2Cl)$, (3.05 g, 78% yield). B.p.: 45°C/20 mmHg. $n_D^{20}$: 1.3930. NMR ($\delta$, ppm) ($C_6H_6$) 4.10 (m, Ge—H), 2.83 (d, $J$(H—Ge—CH) 2.5 Hz, $CH_2Cl$), 0.65—1.20 (m, $C_2H_5$).

*EtGeH(Cl)(CH₂Cl)*

Insertion of carbene (obtained from Cu catalysed decomposition of $CH_2N_2$) in the Ge—Cl bond of $EtGeCl_3$ according to the method of Seyferth and Rochow [26], leads to $EtGeCl_2(CH_2Cl)$ (53% yield). B.p.: 87°C/40 mmHg.

The reduction of $EtCl_2Ge(CH_2Cl)$ (7 g, 0.031 mol) using $LiAlH_4$ (0.6 g, 0.016 mol) and ether (0°C) leads after hydrolysis and ether extraction to $EtH_2GeCH_2Cl$. Purified by distillation, (4.05 g, 84% yield). B.p.: 102°C. NMR ($\delta$, ppm): ($C_6D_6$) 4.33 (m, $GeH_2$), 2.80 (t, $J$(H—Ge—CH) 2.5 Hz, $CH_2$).

$ClCH_2OCH_3$ (2.10 g, 0.026 mol) is added dropwise to $EtGeH_2CH_2Cl$ (4.05 g, 0.026 mol). The reaction is initiated using a catalytic amount of $AlCl_3$. The reaction is followed by GLC and stopped by HCl (12 $N$) hydrolysis when traces of $EtGeCl_2(CH_2Cl)$ appear. The mixture is extracted with pentane. The pentane solution is dried over $Na_2SO_4$ and distilled leading to $EtGeH(Cl)(CH_2Cl)$, (2.24 g, 46% yield). B.p.: 80°C/45 mmHg. NMR ($\delta$, ppm): ($C_6D_6$) 5.38 (m, Ge—H), 2.85 (d, $J$(H—Ge—CH) 2.5 Hz $CH_2$).

*PhMeGeH(CH₂Cl).*

A solution of PhMeGeHCl in ether (7 g, 0.034 mol) is added dropwise at —90°C to freshly prepared $CHCl_2Li$ (0.035 mol). The mixture is stired for 2 h at —90°C and then warmed up to room temperature. After hydrolysis and pentane extraction the solution obtained is dried over $Na_2SO_4$; its distillation leads to $PhMeGeH(CHCl_2)$, (3.66 g, 42% yield). B.p.: 60—66°C/2 × $10^{-2}$ mmHg. NMR ($\delta$, ppm): ($C_6D_6$) 4.80 (m, Ge—H), 5.24 (d, $J$(H—Ge—CH) 2.5 Hz, CH), 0.48 (d, $CH_3$).

$Bu_3SnH$ (4.24 g, 0.0146 mol) is added to $PhMeGeH(CHCl_2)$ (3.66 g, 0.0146 mol). The reaction is initiated by UV irradiation (248—436 nm, 15 min). Distillation of the mixture obtained leads to $PhMeGeH(CH_2Cl)$, (2.15 g, 68% yield) B.p.: 65—70°C/0.2 mmHg. NMR ($\delta$, ppm) 4.72 (m, Ge—H), 3.0 (d, $J$(H—Ge—CH) 2.5 Hz, $CH_2$), 0.48 (d, $CH_3$).

IR spectra were measured on Zeiss UR-20 spectrophotometer. Heptane solutions of the investigated compounds (concentration 0.08—0.12 mol/l) were used to obtain the spectra. Graphical separation of the absorption bands corresponding to coordinated ($v_c$) and "free" ($v_f$) was performed to determine the concentration of coordinated ($C_c$) and "free" ($C_f$) molecules (Fig. 1). The concentration of "free" form molecules was determined by the equation $C_f = \int D(v_f)dv \times 1/A_f L$ [28], where $\int D(v_f)dv$ is the integrated absorbance of the $v_f$(Ge—H) absorption bands (cm$^{-1}$); $A_f$ is the integrated intensity of the $v_f$(Ge—H) absorption bands, (mol$^{-1}$ l cm$^{-2}$); $L$ is the cell path (cm). The integrated intensities of the absorption bands of the coordinated form ($A_c$) and the $\int D(v_f)dv$ values were determined by the calculated Iogansen method [28]. The temperature dependence of the integral absorbance of absorption bands corresponding to molecules of the "free" and coordinated forms was studied to measure $-\Delta H$.

The purity of investigated compounds was checked by GLC.

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