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DIVALENT GERMANIUM SPECIES AS STARTING MATERIALS AND INTERMEDIATES IN ORGANO GERMANIUM CHEMISTRY

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CONTENTS

I. INTRODUCTION AND NOMENCLATURE

The considerable interest devoted to carbene chemistry due to the importance of divalent carbon species in organic chemistry[1] has given rise to the development of the study of the divalent species of Group IVb. Silylene chemistry is notably developed[2,1,3,4], but the chemistry of stannylenes[3,5] remains rather limited, mainly due to the low stability of these intermediates and to their strong tendency to polymerize which limits their use for organometallic synthesis. Likewise, only few papers can be found in the field of the dialkyl- or diaryllead compounds[6].

The chemistry of the germylenes, bivalent germanium derivatives, was oriented until recently essentially toward the study of the dihalogermylenes, GeX_2 (X = Cl, Br, I)[3]. Some diorganogermylenes, R_2Ge, which can be rather readily polymerized to linear or cyclic polygermanes also had been reported.

The purpose of this paper is to discuss the important developments of the chemistry of "germylenes", divalent germanium species, as starting products and intermediates in organometallic synthesis, focusing upon the most recent aspects of this chemistry which has developed vigorously in the last years.

In this paper, we have gathered the available information concerning dihalogermylenes, GeX_2 (X = F, Cl, Br, I), which were the first known and studied divalent species of germanium (especially $GeCl_2$ from trichlorogermane $HGeCl_3$), mixed organogermylenes RGeX (R = alkyl, aryl; X = halogen, alkoxy, hydrogen, GeR_3) characterized more recently,[7] diorganogermylenes R_2Ge and germylene GeH_2 itself. After description of the synthetic methods leading to these intermediates, we will in particular analyze the reactions that proceed via such "carbene" analogs, such as insertion on σ single bonds, addition to carbon–carbon multiple bonds and also the reducing and catalytic properties linked to their electrophilic Lewis-acid character.

The study of divalent species such as Ge–O, $Ge(OH)_2$, Ge–S, Ge–NH, whose applications are rare in organometallic synthesis, has not been developed particularly.

The general term of "germylene"[7], usually accepted by most recent authors to designate the divalent germanium species, is used in this review by analogy with the term "silylene"[2] proposed for the divalent silicon intermediates. For the pure inorganic species, the binary-type names (*e.g.* GeF_2 (germanium difluoride), $GeCl_2$ (germanium dichloride) etc.) also are currently used.

II. METHODS OF PREPARATION, STRUCTURE AND PHYSICAL PROPERTIES

The reactions used for the preparations of germylenes can be divided into two general methods:

(a) Reduction of halogermanes such as tetrahalogermanes to give dihalogermylenes by the action of germanium metal or other strong reducing agents. Dihalodiorganogermanes can be reduced to diorganogermylenes with alkali metals.

(b) α-Eliminations on germanium, by the thermal decomposition of appropriate substrates. Hydroalkoxygermanes, hydrohalogermanes or halodi (or poly)germanes, seem to be the most applicable precursors for many germylenes, particularly for the unsymmetrical divalent species, RR'Ge.

Some other specific methods also have been described but these will be discussed in the appropriate section below.

A. *Dihalogermylenes*

1. *Germanium difluoride*

Germanium difluoride has been prepared by the reduction of germanium tetrafluoride with germanium metal[8,9] in the range of 150–300°

$$Ge + GeF_4 \rightarrow 2\,GeF_2$$

Germanium metal and hydrogen fluoride in a sealed vessel at 225° yielded a mixture of GeF_2 and GeF_4[10]. When stoichiometric amounts of reactants were used, this method served as a simple, high-yield synthesis of GeF_2[11]:

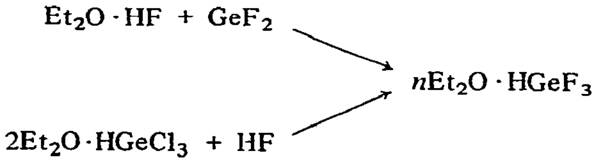
$$Ge + 2\,HF \rightarrow GeF_2 + H_2 \quad (93\%\ \text{yield})$$

GeF_2 is a white solid, m.p. 110°. Crystals of germanium difluoride are orthorhombic[9,12]. GeF_2 possesses strong reducing properties. Above 160° it decomposes into germanium tetrafluoride and germanium monofluoride[9]:

$$GeF_2 \rightarrow GeF_4 + (GeF)_n$$

GeF_2 forms complexes with dioxane $(C_4H_8O_2)_x \cdot GeF_2$ ($x = 0.92$-0.95) and dimethyl sulfoxide[11].

The $HGeF_3$-ether complex was prepared by dissolving germanium difluoride in an ether solution of HF or by passing HF through the $HGeCl_3$-ether complex[13,14]:



$$Et_2O \cdot HF + GeF_2 \rightarrow nEt_2O \cdot HGeF_3$$
$$2Et_2O \cdot HGeCl_3 + HF \rightarrow nEt_2O \cdot HGeF_3$$

GeF_2 readily forms the GeF_3^- ion and its salts (*e.g.* $CsGeF_3$)[11].

No reaction of GeF_2 with organic compounds has been described in the literature. It seems likely that GeF_2 can undergo reactions which are comparable with those of the other germanium dihalides and silicon difluoride[15].

2. *Germanium dichloride*

Various methods for obtaining $GeCl_2$ have been described in the literature. One of the first involved the action of germanium tetrachloride on metallic germanium at 350–400°[16,17].

$$Ge + GeCl_4 \rightleftharpoons 2GeCl_2 \qquad (1)$$

$GeCl_2$ sublimed and deposited as a yellow-white solid. The same reaction has been carried out again by Kochubeev[18] who studied the equilibrium (1). Germanium dichloride can be obtained by low temperature distillation of $HGeCl_3$[19-21] or by careful evaporation of the etherate $2Et_2O \cdot HGeCl_3$ under vacuum[22-24].

$$2Et_2O \cdot HGeCl_3 \xrightarrow{T^\circ} \frac{1}{x}(GeCl_2)_x + 2Et_2O \cdot HCl$$

In these preparations, the polymeric form $(GeCl_2)_x$ appeared to contain some polymeric subchlorides $(Ge_2Cl_3)_x$ and $(GeCl)_x$ and was obtained in the form of a light yellow amorphous or finely crystalline powder with Ge/Cl ratio = 1/1.5–1.6, soluble in acetone but insoluble in most other solvents. The action of chlorine, hydrolysis and the action of H_2S on $(GeCl_2)_x$ led, respectively, to $GeCl_4$, GeO and GeS[16,22]. The strong polarization of the germanium-hydrogen bond of trihalogermanes and its etherates may explain the facility with which formation of GeX_2 takes place. The equations below were proposed for such decomposition:

$$HGeX_3 \rightleftharpoons H^+ + GeX_3^-$$
$$(R_2O \rightarrow H \cdots OR_2)^+ GeX_3^-$$
$$GeX_3^- \rightarrow GeX_2 + X^-$$

In contrast to the $\overset{\delta^+}{\geq Si}-\overset{\delta^-}{H}$ polarization in $HSiCl_3$, the $\overset{\delta^-}{\geq Ge}-\overset{\delta^+}{H}$ polarization in $HGeCl_3$ can be explained by the higher electronegativity of germanium[25-27]. A complex of $GeCl_2$ monomer with dioxane is formed by the action of dioxane on $HGeCl_3$[28].

$$HGeCl_3 + C_4H_8O_2 \rightarrow C_4H_8O_2 \cdot GeCl_2 + HCl$$

The crystal structure of this complex, determined by X-ray analysis, corresponded to a monoclinic system in which monomeric $GeCl_2$ units are coordinated with oxygen atoms of two different dioxane molecules, giving $[-GeCl_2-O-C_4H_8-O-]$ chains with a Cl-Ge-Cl bond angle of 94.6° and an O-Ge-O angle of 180°[29]. The germanium atom in the $GeCl_2$ unit of this complex is in a singlet state corresponding to the electronic ground state configuration $4s^2, 4p^2$ [30,31], similar to the ground state of carbon in "singlet" dichlorocarbene.

$GeCl_2$ also was formed by oxidation of trichlorogermane by silver oxide or oxygen[32]:

$$4HGeCl_3 \xrightarrow{O_2} 2GeCl_2 + 2GeCl_4 + 2H_2O$$

and by the partial reduction of $GeCl_4$ by Et_3GeH[33,34].

Germanium dichloride can be produced by the action of organomethoxygermanes on $HGeCl_3$; two possible mechanisms have been considered in the reaction of $HGeCl_3$ with Bu_3GeOMe[35], which gave a yellow solid form of $GeCl_2$ at higher temperature.

$$\begin{tikzcd}[column sep=small] (I) \quad Bu_3GeOMe + HGeCl_3 \arrow[r] & Bu_3GeGeCl_3 + MeOH \arrow[d] \\ & Bu_3GeCl + GeCl_2 \end{tikzcd}$$

$$HGeCl_3 \rightleftharpoons HCl + GeCl_2$$
$$Bu_3GeOMe + HCl \rightarrow Bu_3GeCl + MeOH$$

$$(II) \quad Cl_3GeH \xrightarrow[-R_3GeCl]{R_3GeOMe} Cl_2GeH(OMe) \longrightarrow GeCl_2 + MeOH$$

$$(R = Et, Ph)$$

Such an α decomposition of a very unstable methoxydichlorohydrogermane formed by a Cl/OMe exchange reaction[36] seems to be more probable in view of our studies on the methoxyhalohydrides of germanium.

The germanium dichloride isolated in this reaction when external heating is not applied, appeared in liquid form (probably associated with methanol). This derivative did not display a Ge-Ge band in the infrared spectrum. On being heated in an inert atmosphere, the liquid form gave a yellow solid identical to the product obtained by direct decomposition of trichlorogermane[19-21] or its etherates[22-24].

The action of the phenyldihalogermanes, PhX_2GeH, on trihalomethoxygermanes led, via a hydrogermolysis reaction, to the unstable phenylpentahalodigermanes which decomposed with quantitative formation of phenyltrihalogermanes and dihalogermylenes[37]:

$$PhX_2GeH + X_3GeOMe \rightarrow PhX_2GeGeX_3 + MeOH$$
$$PhX_2GeGeX_3 \downarrow \; PhGeX_3 + GeX_2 \quad (X = Cl \text{ or } Br)$$

The $GeCl_2$ and $GeBr_2$ thus isolated were liquid and associated with part of the methanol formed in the hydrogermolysis.

The insertion of ethyl-[38] and phenylchlorogermylenes[39] into the Ge-X bonds of the germanium tetrahalides which gives the very unstable pentahalogenated digermanes offers an interesting approach to the dihalogermylenes which were obtained in a high purity state in almost quantitative yields:

$$RGeCl + GeX_4 \rightarrow R(Cl)XGeGeX_3 \rightarrow RX_2GeCl + GeX_2$$
$$(R = Et, Ph; X = Cl, Br, I)$$

In particular, germanium dichloride, which was obtained with traces of methanol via the decomposition of $Cl_2GeH(OMe)$[36] could be prepared in this way in a "liquid form" without traces of methanol; the elementary analysis (found: Cl, 48.85; calcd ∴ 49.41%) corresponds to the stoichiometric formula $GeCl_{1.95}$[38]; IR analysis showed the absence of a Ge–Ge bond in this pure $GeCl_2$.

3. Germanium dibromide

$GeBr_2$ can be isolated by thermal vacuum dissociation of tribromogermane or via the action of zinc on a mixture of germanium tetrabromide and tribromogermane[20]. $GeBr_2$ was also obtained by distillation of an ether solution of tribromogermane containing hydrobromic acid or preferably a solution of $HGeBr_3$ in hydrobromic acid[40,41].

$$Ge(OH)_2 \xrightarrow[\text{ether}]{HBr} Et_2O \cdot HGeBr_3 \xrightarrow{\text{distil.}} GeBr_2 + HBr$$

Curtis and Wolber[42] recently described a new method for the preparation of $GeBr_2$ utilizing germanium and either bromine or germanium tetrabromide. The action of bromine on germanium powder of 350° gave 38% $GeBr_2$ and 39% germanium tetrabromide and reaction of $GeBr_4$ with germanium at 400° gave 51% germanium dibromide. Germanium dibromide was obtained as pale cream-coloured monoclinic crystals melting at 143–144° in vacuo. At 295°, the molten dibromide rapidly deposited a germanium mirror via thermal disproportionation[42,20]:

$$2GeBr_2 \xrightarrow{295^\circ} Ge + GeBr_4$$

In nonpolar solvents the disproportionation occurred at lower temperature to give a germanium subbromide:

$$GeBr_2 \xrightarrow[\text{toluène}]{110°} GeBr_{0.85} + GeBr_4$$

Also, $GeBr_2$ as well as GeI_2 were obtained in a state of high purity by decomposition of the organopentahalodigermanes formed by insertion of RGeCl into GeX_4 (X = Br, I) (R = Et or Ph)[38,39].

$GeBr_2$ is scarcely soluble in benzene, toluene and hydrocarbons, but it dissolves in alcohol and acetone to give colourless solutions with strong reducing power. Its hydrolysis with water leads to the hydrated germanous hydroxide $Ge(OH)_2$.

4. *Germanium diiodide*

The much studied germanium diiodide is formed in many reactions:

(a) the action of iodine on metallic germanium, as by-product in the preparatión of GeI_4. At high temperature the dissociation of tetraiodide gives GeI_2[43]:

$$GeI_4 \xrightarrow{440°} GeI_2 + 2I$$

(b) the action of germanium tetraiodide vapors on the metal in a range of 370–600°[20].

(c) the reaction of the germane, GeH_4, with HI acid in the presence of aluminium bromide[44].

(d) the addition of an acid solution of potassium iodide to an acid solution of germanium dichloride[45]:

$$GeCl_2 + 2KI \rightarrow GeI_2 + 2KCl$$

(e) the action of methyl iodide on a germanium dichloride solution[45]:

$$2CH_3I + GeCl_2(HCl) \rightarrow GeI_2 + 2CH_3Cl$$

(f) the reduction of germanium tetraiodide by hydrazine[46]:

$$2GeI_4 + N_2H_4 \rightarrow 2GeI_2 + N_2 + 4HI$$

(g) GeI_2 was formed in appreciable quantity in the action of the alkyl iodides on trichlorogermane or its etherates[47,48].

The most frequently used methods of preparation are, however:

(h) the partial reduction of germanium tetraiodide with hypophosphorous acid (75% yield)[49]:

$$GeI_4 + H_2O + H_3PO_2 \rightarrow GeI_2 + H_3PO_3 + 2HI$$

(i) the treatment of the germanous hydroxide, $Ge(OH)_2$, with concentrated hydroiodic acid[50,51]. The germanous hydroxide was obtained by reduction of $GeCl_4$ with hypophosphorous acid and precipitation with amonia[50] or by reduction of the germanium dioxide by H_3PO_2[51].

(j) Flood, Foster and Pietrusza[52], following a method described previously by Johnson, Morey and Kott[53], made GeI_2 from germanium monosulfide and hydrogen iodide:

$$GeS + 2HI \rightarrow GeI_2 + H_2S$$

(k) Mironov and Gar prepared germanium diiodide by the exchange reaction of the chlorine in $HGeCl_3$ for iodine by action of hydroiodic acid on trichlorogermane or its etherates[40,41]:

$$HGeCl_3 \xrightarrow{3HI} [HGeI_3] \rightarrow GeI_2 + HI$$

Germanium diiodide appeared in the form of stable yellow crystals at normal temperature and in dry air. The structure is hexagonal and identical with that of cadmium iodide[50,51] Germanium diiodide is insoluble in hydrocarbons, slightly soluble in chloroform and carbon tetrachloride. It can be recrystallized from a concentrated solution of hydroiodic acid.

Germanium diiodide was found to be completely ammonolysed in liquid ammonia to germanous imide[53]:

$$GeI_2 + 3NH_3 \rightarrow GeNH + 2NH_4I$$

Germanous imide is readily hydrolysed

$$GeNH + 2H_2O \rightarrow Ge(OH)_2 + NH_3$$

and reacts with oxygen to give GeO_2[53].

5. Phthalocyanine germanium(II)

Phthalocyaninegermanium(II), PcGe, has been recently described[54]. This compound exhibits the typical phthalocyanine polymorphism with α- and β-modification forms.

PcGe was obtained by reduction of $PcGeCl_2$ with sodium borohydride, sodium borodeuteride, anhydrous stannous chloride (β-PcGe) or with phenylgermane (α-PcGe). In contrast to PcSn, PcGe was not oxidized to Ge^{IV} by bromine, iodine and hydrogen peroxide. Germanium(II) is aparently stabilized by the ring system[54].

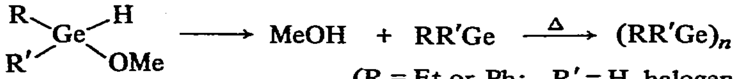
B. Mixed germylenes: Organohalo-(hydro-or alkoxy-)germylenes and organogermylenes with Ge–Ge bond

Methoxyhydrogermanes are unstable and Griffiths and Onyszchuk in the case of methylmethoxygermane[55] or Gibbon *et al.*[56] in the case of methoxygermane observed decomposition with formation of a germanium polymer and elimination of methanol

$$x\mathrm{Me(MeO)GeH_2} \rightarrow x\mathrm{MeOH} + (\mathrm{MeGeH})_x$$

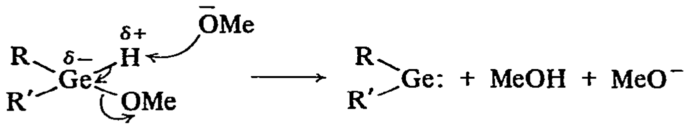
$$x\mathrm{MeOGeH_3} \rightarrow x\mathrm{MeOH} + (\mathrm{GeH_2})_x$$

Among the organomethoxygermanes of the types $R_2(MeO)GeH$ (I), $R(MeO)GeH_2$ (II), $R(MeO)(X)GeH$ (III), $R(MeO)_2GeH$ (IV) (R = Et, Ph; X = halogen), only the compounds of type I and II are stable in the absence of base in the medium[7,57]. With derivatives of type III and IV a quick decomposition was noted, with release of methanol and formation of germylenes, which condensed to a polygermane.

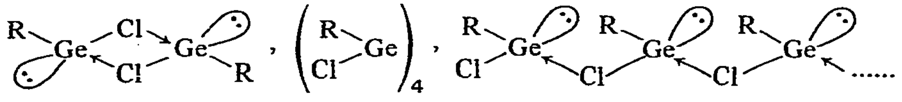


(R = Et or Ph; R′ = H, halogen or OMe)

An α-elimination process serves to explain this decomposition which is strongly catalyzed by the bases, in particular, by alkoxide ion:



This first-order decomposition, which is favored by the polarity of the solvent, is very fast in a protic solvent such as MeOH and appears to be autocatalyzed by the methoxide ions formed even in an inert solvent (pentane)[7]. The α-decomposition depends also on the polarity of Ge-hydrogen bond of the starting methoxyhalohydride compounds, and increasing rates of decomposition were noted with enhancement of the protonic character of hydrogen bonded to germanium. Thus, the stability of organoalkoxygermanes decreases in the order: $Et_2(MeO)GeH \gg Et(MeO)GeH_2 \sim Ph(MeO)GeH_2 \sim Ph_2(MeO)GeH > Et(MeO)(X)GeH \sim Ph(MeO)(X)GeH > Et(MeO)_2GeH \sim Ph(MeO)_2GeH > Cl_2(MeO)GeH$. The germylenes thus formed at room temperature condensed to give amorphous, pasty polymers in the case of R′ = H or Ph (the infrared spectrum of these substances shows a ν(Ge–Ge) band in the range of 290 cm^{-1}) or a viscous oil which does not contain Ge–Ge bonds (by IR) and which is stable at normal temperature if R′ = Cl, OMe. In this latter case, the stabilization of the germylene seems to be due to an intermolecular association in the form of dative bonding involving the lone pairs of the halogen or oxygen atoms and the vacant $3p$ (or $4d$) orbitals of Ge in singlet state. Thus the chlorogermylenes are "associated", but without Ge–Ge bonds. They were found to be dimeric (molecular weight of EtGeCl determined by ebullioscopy in benzene), tetrameric (cryoscopy in benzene) or oligomeric:



This hypothesis seems to be confirmed by IR-data obtained in the germanium–chlorine absorption region. We noted that on heating freshly prepared PhGeCl germylene the 400 cm^{-1} absorption attributed to Ge–Cl bond in the "associated" form disappeared and an absorption at 418 cm^{-1} due to the free Ge–Cl vibration appeared, indicating formation of the Ge–Ge bonded $(PhGeCl)_n$. In comparison, the Ge–Cl stretch is located at 420, 420 and 445 cm^{-1}, respectively, in $PhGeCl_3$, Ph_2GeCl_2 and Ph_3GeCl. In the same manner, the 380 cm^{-1} Ge–Cl absorption of "associated" EtGeCl disappeared on heating and was replaced by the corresponding Ge–Cl band at 400 cm^{-1} of $(EtGeCl)_n$. The low position of ν(Ge–Cl) at 400 cm^{-1} (380 cm^{-1} for PhGeCl and EtGeCl) can be explained by the lower vibration energy of the Ge–Cl bond when chlorine participates to dative bonding with another Ge atom[155].

The polygermanes produced by heating the respective germylenes can be reduced to polyhydrogermanes[7]

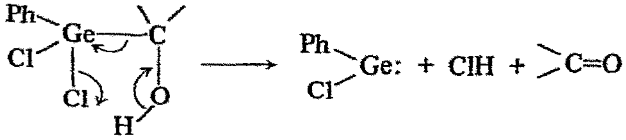
$$n\mathrm{RGeCl} \xrightarrow{\Delta} (\mathrm{RGeCl})_n^{\cdot} \xrightarrow{\mathrm{LiAlH_4}} (\mathrm{RGeH})_n$$

ν(GeH) 2015 cm^{-1}

The same type of polymer, $(\mathrm{RGeH})_n$, can be obtained by a Wurtz reaction of a dichlorogermane and lithium or magnesium mercury amalgam[58,59]:

$$\mathrm{R(Cl)_2GeH} \xrightarrow[0°\mathrm{C}]{\mathrm{Li/Hg}} [\!-\!\overset{\mathrm{Ph}}{\underset{\mathrm{H}}{\mathrm{Ge}}}\!-\!]_n$$

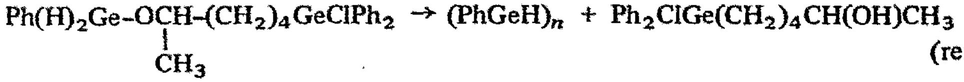
α-Chlorogermyl alcohols are rather unstable thermally. Their decomposition takes place via intramolecular elimination of hydrogen chloride with a simultaneous formation of carbonyl derivatives and germylenes[58,60–62]:



The mixed germylenes RGeX (X = halogens, H, OMe), were formed in many decomposition reactions of di- or polygermanes. These are mostly reversible reactions at normal temperature, for example:

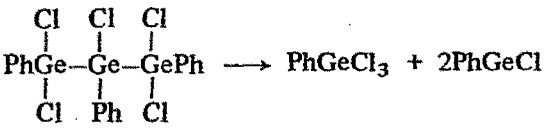
$$\mathrm{PhX_2GeGeX_2Ph} \rightleftarrows \mathrm{PhGeX_3} + \mathrm{PhGeX}\ (\mathrm{X = Cl, Br}) \qquad \text{(refs. 58, 37, 39)}$$

$$\mathrm{PhCl_2GeGe(Ph)_2(CH_2)_4CH(OH)CH_3} \rightarrow \mathrm{PhGeCl} + \mathrm{Ph_2ClGe(CH_2)_4CH(OH)CH_3} \qquad \text{(ref. 37)}$$



$$\mathrm{Ph(H)_2Ge\text{-}O\underset{CH_3}{C}H\text{-}(CH_2)_4GeClPh_2} \rightarrow (\mathrm{PhGeH})_n + \mathrm{Ph_2ClGe(CH_2)_4CH(OH)CH_3} \qquad \text{(ref. 37)}$$

$$\mathrm{Ph(MeO)_2GeGe(OMe)_2Ph} \rightarrow \mathrm{PhGe(OMe)_3} + \mathrm{PhGeOMe} \qquad \text{(ref. 37)}$$



$$\mathrm{Ph\overset{Cl}{\underset{Cl}{Ge}}\!-\!\overset{Cl}{\underset{Ph}{Ge}}\!-\!\overset{Cl}{\underset{Cl}{Ge}}Ph} \longrightarrow \mathrm{PhGeCl_3} + 2\mathrm{PhGeCl} \qquad \text{(ref. 39)}$$

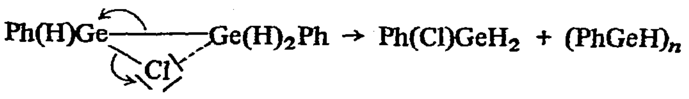
$$\mathrm{PhCl_2GeGeH_2Ph} \xrightarrow{T°} \mathrm{Ph(Cl)GeH_2} + (\mathrm{PhGeCl})_n \qquad \text{(ref. 63)}$$

$$PhCl_2GeGe(Cl)(H)Ph \xrightarrow{T^\circ} PhCl_2GeH + (PhGeCl)_n \qquad \text{(ref. 63)}$$

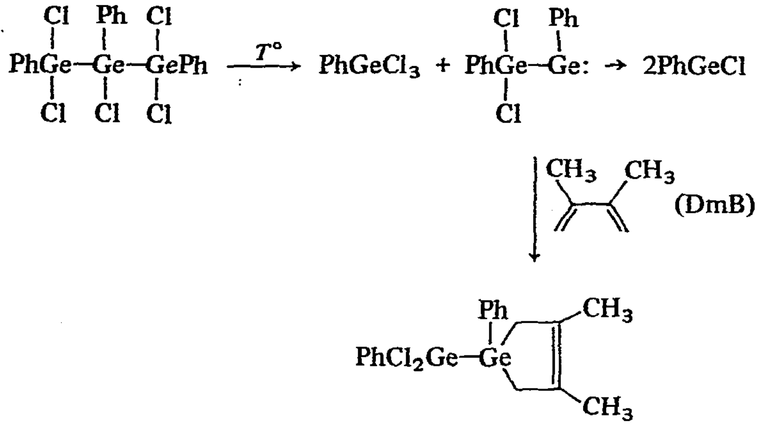
$$Ph(Cl)HGeGe(H)_2Ph \xrightarrow{T^\circ} Ph(Cl)GeH_2 + (PhGeH)_n \qquad \text{(ref. 63)}$$

$$Ph(Cl)(H)GeGe(H)(Cl)Ph \xrightarrow{T^\circ} PhCl_2GeH + (PhGeH)_n \qquad \text{(ref. 63)}$$

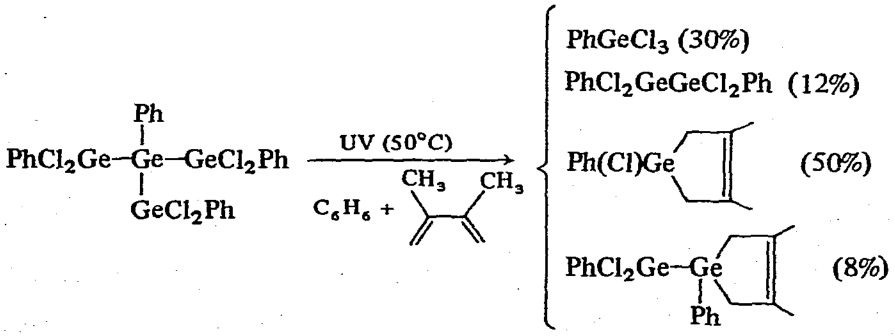
These α-eliminations probably begin by intramolecular coordination of a chlorine atom with a germanium atom:



In the decomposition by α-elimination of 1,1,2,3,3-pentachloro-1,2,3-triphenyltrigermane, the phenyl(phenyldichlorogermyl)germylene formed has been trapped[95]:



The phenyl(phenyldichlorogermyl)germylene also has been generated by UV irradiation of a benzene solution of phenyltris(phenyldichlorogermyl)germane[95]:



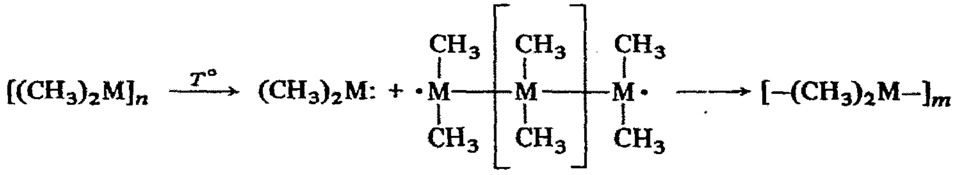
C. *Diorganogermylenes R_2Ge*

Like their silicon analogs[2], the diorganogermylenes may occur as intermediates in the reduction of diorganodihalogermanes by metals in various aprotic solvents. Dimethyldichlorogermane, like $(CH_3)_2SiCl_2$, reacts with lithium in THF, giving essentially the cyclic hexamer $[(CH_3)_2Ge]_6$, m.p. 211–213° (yield 80%). This polymer is readily soluble in common organic solvents. At lower temperature (about 0°), the yield of poly(dimethylgermylene) $[(CH_3)_2Ge]_n$ is about 50%. The formation of these polymeric germanium products can be rationalized in terms of the formation of dimethylgermylene[64–66]:

$$n(CH_3)_2GeCl_2 \xrightarrow[-n\,LiCl]{2n Li} n(CH_3)_2Ge(Li)Cl \xrightarrow{-nLiCl}$$

$$n[(CH_3)_2Ge] \rightarrow [(CH_3)_2Ge]_6 + [(CH_3)_2Ge]_n$$

The structures of the cyclic and linear polymers of dimethylsilylene and germylene and their thermal decomposition were studied by Nefedov *et al.*[67]. The pyrolysis of these polymeric materials at about 350–400° resulted mainly in the scission of metal-metal bonds and the formation of monomeric, dimeric and polymeric diradicals:



$$[(CH_3)_2M]_n \xrightarrow{T^\circ} (CH_3)_2M: + \cdot\overset{CH_3}{\underset{CH_3}{M}}-\left[\overset{CH_3}{\underset{CH_3}{M}}-\right]\overset{CH_3}{\underset{CH_3}{M}}\cdot \longrightarrow [-(CH_3)_2M-]_m$$

A UV spectral study of the $(R_2Si)_n$ and $(R_2Ge)_n$ species was carried out by Nefedov *et al.*[68].

Diethylgermylene, Et_2Ge, was also formed in the reaction of Et_2GeCl_2 with lithium in THF, but an insoluble polymer $(Et_2Ge)_n$ is the final product[66]. In the action of potassium on Bu_2GeCl_2 in HMPT, the intermediate formation of dibutylgermylene can be assumed[69,35]:

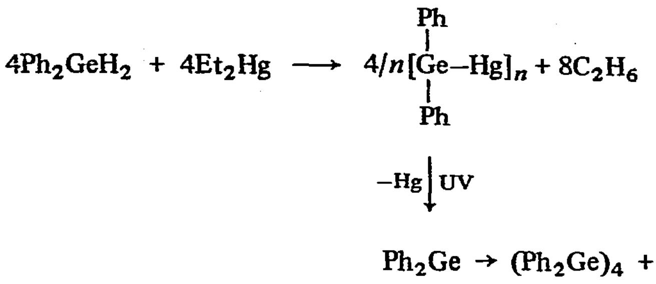
$$Bu_2GeCl_2 \xrightarrow{2\,K} [Bu_2Ge] \xrightarrow{2\,K} Bu_2GeK_2$$

Reaction of sodium with diphenyldichlorogermane in boiling xylene gave both octaphenylcyclotetragermane $(Ph_2Ge)_4$ (32% yield) and a yellow resinous material with molecular weight of about 900 (containing 30–32% germanium; Ph_2Ge requires 32%)[70,71].

Moreover, diphenyldichlorogermane reacted with lithium in THF, or with sodium naphthalenide in 1,2-dimethoxyethane (DME), giving decaphenylcyclopentagermane and dodecaphenylcyclohexagermane[72–74]. The reactions probably proceed via diphenylgermylene

$$Ph_2GeCl_2 \xrightarrow[THF]{Li} (Ph_2Ge) \rightarrow (Ph_2Ge)_5 + (Ph_2Ge)_6 + (Ph_2Ge)_n$$

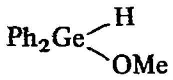
The reaction of diphenylgermane with diethylmercury led to polymeric diphenylgermylene and octaphenylcyclotetragermane[73,71]:



$$4Ph_2GeH_2 + 4Et_2Hg \longrightarrow 4/n[Ge(Ph)_2\text{–}Hg]_n + 8C_2H_6$$

$$\xrightarrow[-Hg]{UV} Ph_2Ge \rightarrow (Ph_2Ge)_4 + (Ph_2Ge)_n$$

Diphenylgermylene also was formed in the decomposition of $Ph_2GeH(OMe)$ by α-elimination



$$Ph_2Ge(H)(OMe) \longrightarrow Ph_2Ge + MeOH \qquad \text{(ref. 7, 58)}$$

Polymers of diphenylgermylene, $(Ph_2Ge)_n$, also were formed by the action of phenyllithium, PhMgBr or Ph_3Al on GeI_2[75,76].

Attempts to alkylate $HGeCl_3$ or its etherates with Grignard reagents or organolithium compounds have been unsuccessful. In all cases, telomers $R[GeR_2]_nR$, $n \geqslant 2$, were formed[77,22,23], together with small quantities of cyclopolymers $[GeR_2]_n$ $n = 4$ or 6. The participation of dichlorogermylene due to the equilibrium $HGeCl_3 \rightleftharpoons HCl + GeCl_2$ seems a reasonable explanation[22,23].

Diethyl and di-*n*-butylgermylene were formed by the action of the respective dialkylmercury on GeI_2[78].

Vyazankin *et al.* reported that hexaethyldigermane disproportionates on being heated at 200° in the presence of $AlCl_3$ or $AlBr_3$ according to[79]:

$$Et_3Ge\text{–}GeEt_3 \xrightarrow{AlX_3} Et_4Ge + (Et_2Ge)_x$$

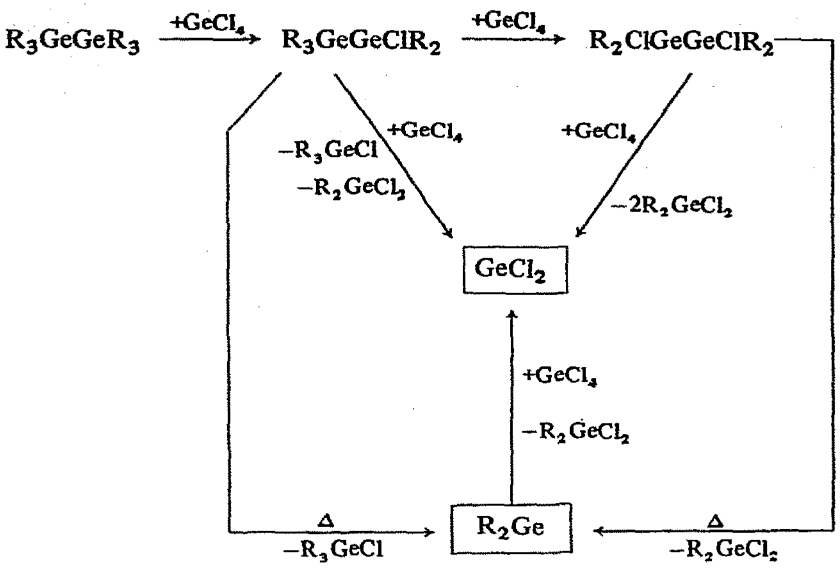
$Et_2ClGeGeClEt_2$ and $Et_3GeGeClR_2$ decompose thermally in similar fashion[80,35]:

$$Et_3GeGeClEt_2 \rightarrow Et_3GeCl + (Et_2Ge)_n$$

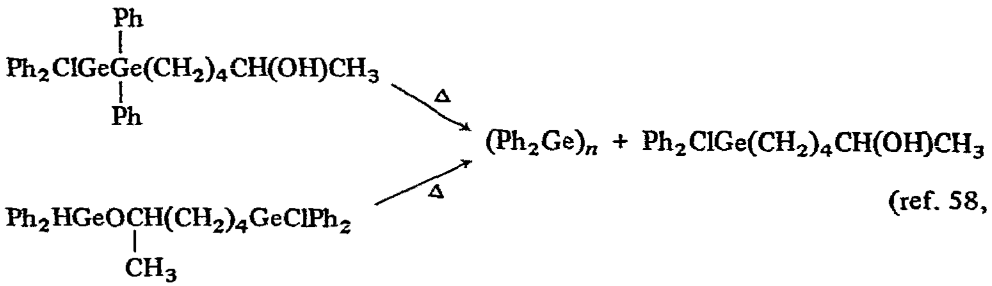
$$Et_2ClGeGeClEt_2 \rightarrow Et_2GeCl_2 + (Et_2Ge)_n$$

In these reactions the formation of intermediate diethylgermylene has been confirmed by characterization of polygermanes $Et_3Ge(GeEt_2)_nGeClEt_2$ ($n = 1$ or 2) which derive from the insertion of Et_2Ge into the Ge–Cl bonds of $Et_3GeGeClEt_2$[35,81].

The formation of divalent germanium species in the hexaalkyldigermane-catalyzed redistribution is shown schematically below[35]:



The formation of diphenylgermylene in the decomposition of many di- or polygermanes has been reported:



(ref. 58, 37)

$$Ph_2(Cl)GeGe(H)Ph_2 \xrightarrow{\Delta} Ph_2(Cl)GeH + (Ph_2Ge)_n \qquad \text{(ref. 63)}$$

$$mPh_2(H)GeGe(H)Ph_2 \xrightarrow{\Delta} mPh_2GeH_2 + (Ph_2Ge)_n \qquad (59)$$

Finally, R_2Ge can be obtained by pyrolysis of 7-germanorbornadienes. The synthesis of a germacyclopentadiene-phenylacetylene adduct has been reported at a meeting[66] and reviewed[3] as a generator of dimethylgermylene, which gave dimethylgermanium polymers and cyclic organogermanium compounds in the presence of ethylene. However preparations and physical properties of these compounds have not yet been published, and it was found more recently[82] in different attempts to prepare the same 7,7-dimethyl-1,2,3,4,5-pentaphenyl-7-germanorbornadiene that this adduct seems to be very unstable. The germacyclopentadienedimethylacetylene dicarboxylate adduct is more stable, and may generate at 50–60° the dimethylgermylene which was characterized by addition to the carbon–carbon triple bond of dimethylacetylene dicarboxylate[82] (*cf.* III B2).

D. Germylene: GeH_2

As in the case of silylene, SiH_2, germylene, GeH_2, has often been invoked as a reactive intermediate. The formation of GeH_2 was reported in 1933 as resulting in the hydrolysis of CaGe by aqueous sulfuric acid[83]. However, these results were refuted in further papers[84,85].

GeH_2 seems to be first characterized in the action of bromobenzene on germylsodium[85]:

$$NaGeH_3 + C_6H_5Br \rightarrow NaBr + C_6H_6 + GeH_2$$

and also in the decomposition of digermane catalyzed by the alkali metal salts such as lithium chloride or lithium hydride[86]:

$$xGe_2H_6 \xrightarrow{LiX} xGeH_4 + \frac{1}{x}[GeH_2]_x$$

In the pyrolysis of Ge_2H_6, germylene has been reported as an intermediate[87], as well as in the pyrolysis of the polygermanes Ge_4H_{10}, Ge_4H_{12}[88]. The GeH_2 was isolated in the form of a polymer. Fensham *et al.* reported the formation of germylene in a study of the mechanism of the decomposition of GeH_4[89].

The reduction of $GeCl_4$ by $LiAlH_4$ in ether leads to a high proportion of GeH_2 in addition to the expected GeH_4. The formation of GeH_2 can be explained by the partial reduction of $GeCl_4$ to $HGeCl_3$ and H_2GeCl_2 followed by the decomposition of these derivatives to $GeCl_2$ which then is reduced by $LiAlH_4$[90].

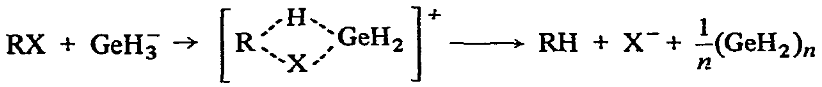
Onyszchuk, Srivastava *et al.* reported the formation of GeH_2 polymer in the decomposition of the adducts of chlorogermane with various amines[91,92]:

$$\equiv N\!: + H_3GeCl \xrightarrow{-78^\circ} \equiv N\!: GeH_3Cl \xrightarrow{> -78^\circ} \equiv N \cdot HCl + (GeH_2)_x$$

and in the thermal decomposition (in the range of 50–200°) of germylisocyanates, isothiocyanates and acetate[92,93]:

$$xGeH_3X \rightarrow (GeH_2)_x + xHX \qquad (X = CN, NCO, NCS, OCOCH_3)$$

Potassium germyl reacts with some organic halides to give mainly the corresponding hydrocarbons and GeH_2 polymer[160]:



$$RX + GeH_3^- \rightarrow \left[R \underset{X}{\overset{H}{\diamond}} GeH_2 \right]^{+} \longrightarrow RH + X^- + \frac{1}{n}(GeH_2)_n$$

Germanium dihydride is readily soluble in liquid ammonia. It appears to be stable in such solutions. It may be crystallized from this solution as a white solid[85]. It decomposes in a complex manner yielding hydrogen, germane, metallic germanium and $(GeH)_x$[85,93,94]:

$$3GeH_2 \rightarrow GeH_4 + 2GeH \quad ; \quad GeH \rightarrow Ge + \tfrac{1}{2}H_2$$

III. GENERAL REACTIVITY OF GERMYLENES

A. Insertion reactions into single bonds

One of the most characteristic reactions of carbenes and their silicon analogues, is their insertion on covalent single bonds[1]. The germylenes exhibit analogous properties due to their "carbene like" character and have been shown to insert into hydrogen-halogen, carbon-halogen, metal-halogen, metal-hydrogen, metal-carbon and metal-metal bonds.

1. Insertions into hydrogen–halogen bonds

The easy reaction of germylenes with hydrogen-halogen bond of the hydrogen halides is illustrated by the balanced reactions observed with trichlorogermane and its etherates; these reactions have been mentioned in many papers[21,3] and references cited therein):

$$HGeCl_3 \rightarrow H^+[GeCl_3]^- \rightleftarrows HCl + GeCl_2$$

$$2Et_2O \cdot HGeCl_3 \rightleftarrows GeCl_2 + 2Et_2O \cdot HCl$$

Treatment of $(GeCl_2)_n$ polymer with hydrogen chloride or its etherates also leads to $HGeCl_3$ or trichlorogermane etherate[23,24]:

$$2Et_2O \cdot HCl + \frac{1}{x}(GeCl_2)_x \rightarrow 2Et_2O \cdot HGeCl_3$$

The action of GeI_2 on hydrogen chloride etherate leads to the mixed etherate $HGeI_2Cl \cdot 2Et_2O$[22-24]. $GeBr_2$ and even GeI_2 seem to exist in equilibrium with tribromogermane[40,41] and triiodogermane[96-98], respectively, in concentrated HBr or HI medium:

$$HGeBr_3 \rightleftarrows GeBr_2 + HBr$$

$$HGeI_3 \rightleftarrows GeI_2 + HI$$

The organohalogermylenes EtGeX and PhGeX in their "associated form" were found to be reactive toward hydrogen chloride in concentrated aqueous solution and insert into the H–Cl bond[7,57,58]:

$$RGeCl + HCl \xrightarrow{80^\circ} R(Cl)_2GeH$$

Reaction of dimethylgermylene polymer $[(CH_3)_2Ge]_n$ or the telomer $CH_3[Ge(CH_3)_2]_nCH_3$, $n \geqslant 2$ with hydrogen chloride at 200–250°, led to formation of $(CH_3)_2GeHCl$ and $(CH_3)_2GeCl_2$[77,23].

2. Insertions into carbon–halogen bonds: (see Table 1)

(*a*) In 1964, Nefedov reported the insertion of $GeCl_2$ into the C–Cl bond of benzyl chloride with formation of $Cl_3GeCH_2C_6H_5$[22]. This reaction has been extended to the case of chloromethyl ether, and its mechanism has been studied[23,24,36]:

$$GeCl_2 + ClCH_2OCH_3 \rightarrow |Cl_3GeCH_2OCH_3$$

The insertion of germanium dichloride (and other germanium dihalides) into polar C-X bond is probably ionic in character and may possibly involve preliminary C-X heterolysis, combination of the halogen anion of organic halide with $GeCl_2$ to form the trihalogermyl

TABLE 1

GeX_2 insertions into C–halogen bonds

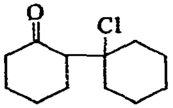
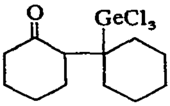
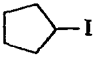
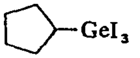
Reactant	*Nature of GeX_2 or X, Y in GeXY*	*Product*	*Yield (%)*	*Ref.*
CCl_4	$GeCl_2 \cdot$ dioxane	CCl_3GeCl_3	73	31
CCl_4	$GeCl_2$	CCl_3GeCl_3	–	38
CCl_4	Et, Cl	CCl_3GeCl_2Et	30	38
$CHCl_3$	$GeCl_2 \cdot$ dioxane	$CHCl_2GeCl_3$	90	31
CH_2Cl_2	$GeCl_2 \cdot$ dioxane	$CH_2ClGeCl_3$	36	31
CH_3Cl	$GeCl_2 \cdot$ dioxane	CH_3GeCl_3	25	31
$n\text{-}C_4H_9Cl$	$GeCl_2 \cdot$ dioxane	$n\text{-}C_4H_9GeCl_3$	49	31
$s\text{-}C_4H_9Cl$	$GeCl_2 \cdot$ dioxane	$s\text{-}C_4H_9GeCl_3$	32	31
$t\text{-}C_4H_9Cl$	$GeCl_2 \cdot$ dioxane	$t\text{-}C_4H_9GeCl_3$	75	31
$t\text{-}C_4H_9Cl$	$GeCl_2$ from $HGeCl_3$ in ether	$t\text{-}C_4H_9GeCl_3$	80	99
$(C_6H_5)_3CCl$	$GeCl_2$ from $HGeCl_3$ in ether	$(C_6H_5)_3CGeCl_3$	77	99
C_6H_5Cl	$GeCl_2 \cdot$ dioxane	$C_6H_5GeCl_3$	37	31
$\alpha\text{-}C_{10}H_7Cl$	$GeCl_2 \cdot$ dioxane	$\alpha\text{-}C_{10}H_7GeCl_3$	70	31
$Cl_2C{=}CHCl$	$GeCl_2 \cdot$ dioxane	$Cl_2C{=}CHGeCl_3$	60	31
$CH_2{=}CH{-}CH_2Cl$	$GeCl_2$	$CH_2{=}CH{-}CH_2GeCl_3$	55	36
$CH_2{=}CH{-}CH_2Cl$	Et, Cl	$CH_2{=}CH{-}CH_2GeCl_2Et$	11	36
$CH_2{=}CH{-}CH_2Cl$	Ph, Cl	$CH_2{=}CH{-}CH_2GeCl_2Ph$	15	36
$CH_3CHClCH{=}CH_2$	$GeCl_2$ from $HGeCl_3$ in ether	$CH_3CH{=}CH{-}CH_2GeCl_3$	66	99
$C_6H_5CH_2Cl$	$GeCl_2$, powder	$C_6H_5CH_2GeCl_3$	54	22, 23, 24
$C_6H_5CH_2Cl$	$GeCl_2 \cdot$ dioxane	$C_6H_5CH_2GeCl_3$	80	28
CH_3OCH_2Cl	$GeCl_2$, powder	$CH_3OCH_2GeCl_3$	56	23, 24
CH_3OCH_2Cl	$GeCl_2$	$CH_3OCH_2GeCl_3$	86	36
CH_3OCH_2Cl	Et, Cl	$CH_3OCH_2GeCl_2Et$	57	36
CH_3OCH_2Cl	Ph, Cl	$CH_3OCH_2GeCl_2Ph$	35	36
CH_3COCH_2Cl	Et, Cl	$CH_3COCH_2GeCl_2Et$	[a]	36
CH_3COCH_2Cl	Ph, Cl	$CH_3COCH_2GeCl_2Ph$	[a]	36
$C_6H_5COCH_2Cl$	Et, Cl	$C_6H_5COCH_2GeCl_2Et$	[a]	36
$C_6H_5COCH_2Cl$	Ph, Cl	$C_6H_5COCH_2GeCl_2Ph$	[a]	36
CH_3COCl	Et, Cl	$CH_3COGeCl_2Et$	[a]	36
CH_3COCl	Ph, Cl	$CH_3COGeCl_2Ph$	[a]	36
$(C_6H_5)_2CHCOCl$	$GeCl_2$	$(C_6H_5)_2CHCOGeCl_3$	45	36
$(C_6H_5)_2CHCOCl$	Et, Cl	$(C_6H_5)_2CHCOGeCl_2Et$	28	36
$(C_6H_5)_2CHCOCl$	Ph, Cl	$(C_6H_5)_2CHCOGeCl_2Ph$	28	36
	$GeCl_2 \cdot$ dioxane		60	100, 101
	$GeCl_2$ from $HGeCl_3$		65	100, 101

TABLE 1–cont.

Reactant	*Nature of GeX_2 or X, Y in GeXY*	*Product*	*Yield (%)*	*Ref.*
CBr_4	$GeBr_2$	CBr_3GeBr_3	30	42
C_2H_5Br	$GeCl_2$	$C_2H_5GeX_3$	60	36
C_2H_5Br	Et, Cl	$(C_2H_5)_2GeClBr$	60	36
n-C_4H_9Br	GeI_2	n-$C_4H_9GeX_3$	[b]	106
$Br(CH_2)_4Br$	GeI_2	$Br(CH_2)_4GeX_3$	[b]	106
$CH_2{=}CH{-}CH_2Br$	$GeBr_2$	$CH_2{=}CH{-}CH_2GeBr_3$	65	40, 41
$CH_3CH{=}CHCH_2Br$	Et, Cl	$CH_3CH{=}CHCH_2GeClBrEt$	80	36
CH_3OCOCH_2Br	Et, Cl	$CH_3OCOCH_2GeX_2Et$	75	36
CH_3I	GeI_2	CH_3GeI_3	100	104
C_2H_5I	GeI_2	$C_2H_5GeI_3$	86	103
n-C_4H_9I	GeI_2	n-$C_4H_9GeI_3$	[b]	106, 97
t-C_4H_9I	GeI_2	t-$C_4H_9GeI_3$	[b]	97
C_6H_5I	GeI_2	$C_6H_5GeI_3$	[b]	106, 97
CF_3I	GeI_2	CF_3GeI_3	43	105
	GeI_2		[b]	97
$CH_2{=}CH{-}I$	GeI_2	$CH_2{=}CH{-}GeI_3$	[b]	97
$CH_2{=}CH{-}CH_2I$	GeI_2	$CH_2{=}CH{-}CH_2GeI_3$	52	97, 98, 107
ICH_2I	GeI_2	ICH_2GeI_3	[b]	97, 106
$I(CH_2)_3I$	GeI_2	$I(CH_2)_3GeI_3$	[b]	97
$I{-}CH{=}CH{-}I$	GeI_2	$I{-}CH{=}CH{-}GeI_3$	[b]	97
CH_3OCH_2I	GeI_2	$CH_3OCH_2GeI_3$	[b]	97, 106
$C_2H_5OCOCH_2I$	GeI_2	$C_2H_5OCOCH_2GeI_3$	[b]	97, 106
I_3GeCH_2I	GeI_2	$I_3GeCH_2GeI_3$	[b]	97
Et_3GeCH_2I	GeI_2	$Et_3GeCH_2GeI_3$	[b]	97
$I_3GeCH{=}CHI$	GeI_2	$I_3GeCH{=}CHGeI_3$	[b]	97

[a] Unstable compounds, which must be characterized by physical analysis and decomposition or further reactions (alkylation, reduction).

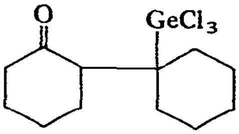
[b] Yield are not given, but generally higher than 80%, according to a private communication of the authors.

anion, $GeCl_2X^-$, which then adds to the corresponding carbonium ion to give the final product.

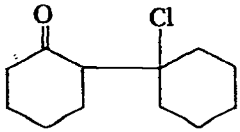
The $GeCl_2 \cdot$ dioxane complex also reacts with benzyl chloride to give an 80% yield of $C_6H_5CH_2GeCl_3$[28].

In the reaction of trichlorogermane with allylic halides and saturated tertiary halides which results in the replacement of halogen by the trichlorogermyl group, Mironov *et al.* considered a reaction course involving the partial or total participation of the $GeCl_2$ insertion reaction into the carbon-halogen bond of the organic halide[99].

The following trichlorogermyl ketone:



was formed on treatment of the dioxane · germanium dichloride complex (or $HGeCl_3$) with 2-(1′-chlorocyclohexyl)cyclohexanone[100,101]:



$GeCl_2$ generated from the same dioxane · $GeCl_2$ complex inserted readily into the C–halogen bonds of different polychloromethanes, alkyl chlorides and aryl halides[30,31]:

$$RX + GeCl_2 \rightarrow RGeCl_2X$$

where R = CCl_3, $CHCl_2$, CH_2Cl, CH_3, *n*–, sec- and tert-C_4H_9, C_6H_5, α-$C_{10}H_7$ (X = Cl or Br).

The authors suggested that the initial step in the reaction is the direct interaction of the divalent species $GeCl_2$ with the organic halide molecule, most probably via the formation of a linear transition state complex of the type (A):

$$GeCl_2\text{–}L + RX \xrightarrow{\Delta} R\cdots X\cdots GeCl_2\cdots L \xrightarrow{-L} (R\cdot + \cdot GeCl_2X) \rightarrow RGeCl_2X^{(A)}$$

(L is the ligand molecule).

In contrast to the polychloromethanes, the polychloroethanes Cl_3CCCl_3, Cl_3CCHCl_2 and $Cl_2CHCHCl_2$ underwent dechlorination reactions with the $GeCl_2$ · dioxane complex, giving mainly $GeCl_4$ and chlorinated ethylenes. This was apparently due to the ease of thermal *β*-decomposition of the initially formed insertion products:

$$Cl_3CCCl_3 \xrightarrow{GeCl_2} Cl_3CCCl_2GeCl_3 \xrightarrow{\Delta} Cl_2C{=}CCl_2 + GeCl_4$$

Insertion of $GeCl_2$ into the C–Cl bond of trichloroethylene occured readily and gave a 60% yield of dichlorovinyltrichlorogermane, $Cl_2C{=}CHGeCl_3$[31]. We have found that the germanium dichloride, $GeCl_2$, in pure "liquid" form, isolated by decomposition of $(CH_3O)Cl_2GeH$[36] inserts into the C–X bonds of ethyl bromide, allyl chloride, methyl bromoacetate and diphenylacetyl chloride in good yield. C–Br bonds were found to be more reactive than the corresponding C–Cl bonds[36].

$$\begin{tikzcd}
MeO(Cl)_2GeH \arrow[r, "-MeOH"] & GeCl_2 \arrow[dr, "RX"] & \\
 & & RGeCl_2X
\end{tikzcd}$$

(X = Br, R = Et, CH_2COOMe)
(X = Cl, R = Allyl, $COCHPh_2$)

In the direct synthesis of methylchlorogermanes by the action of a mixture of CH_3Cl and HCl on metallic germanium, Gorbunov *et al.*[102] postulated the formation of $GeCl_2$ as an intermediate which then, reacts with CH_3Cl, yielding CH_3GeCl_3.

(*b*) Germanium dibromide reacted with carbon tetrabromide to form tribromomethyltribromogermane[42]:

$$GeBr_2 + CBr_4 \rightarrow Br_3CGeBr_3 \quad (30\%\ \text{yield})$$

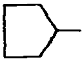
It also reacted vigorously with allyl bromide to give allyltribromogermane[40,41]:

$$GeBr_2 + CH_2{=}CH{-}CH_2Br \rightarrow Br_3GeCH_2CH{=}CH_2$$

With allyl chloride the reaction went partially, with formation of $CH_2{=}CH{-}CH_2GeClBr_2$[41].

(*c*) In contrast to germanium dibromide whose reactions have not been studied extensively, the chemistry of germanium diodide has received much attention, particularly its insertion reactions into the carbon-iodine bond of organic iodides:

$$GeI_2 + RI \rightarrow RGeI_3$$

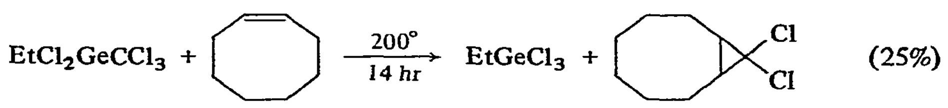
R = Et, Me[103,104], CF_3[105], C_4H_9, C_6H_5, CH_2I, CH_2OCH_3, $CH_2COOC_2H_5$[106,97], $CH_2{=}CH$, $ICH{=}CH$, $CH_2{=}CH{-}CH_2$, $ICH_2CH_2CH_2$, t-C_4H_9, , I_3GeCH_2, Et_3GeCH_2, $I_3GeCH{=}CH$[97].

The insertion reactions of GeI_2 into organic bromides, R-Br (R = C_4H_9, $-(CH_2)_4Br$), also took place in accordance with the same scheme[106]. The insertion of GeI_2 into the C-I bond of allyl iodide also has been reported by other authors[98,107].

(*d*) The mixed germylenes RGeCl (R = alkyl, phenyl) were found to react with organic halides. The insertion of these germylenes into the halogen-carbon bond of β-ethylenic halides (allyl chloride, crotyl bromide), α-halocarbonyl compounds (α-haloketones, α-haloesters), acid chlorides and α-haloethers gave the functionally-substituted α- or β-organopolyhalogermanes[36]. Ethylchlorogermylene reacted with CCl_4 to give ethyl(trichloromethyl)dichlorogermane (30% yield)[38]:

$$EtGeCl + CCl_4 \xrightarrow[4\ \text{days}]{120°} EtCl_2GeCCl_3 + EtGeCl_3$$

This trichloromethylgermane releases dichlorocarbene on thermolysis.



Germanium dichloride gives the same type of insertion reaction into CCl_4. In the reaction of ethylchlorogermylene with carbon tetrabromide, the presumed intermediate, $EtClBrGeCBr_3$, decomposed to ethylchlorodibromogermane, during the distillation but several attempts to intercept CBr_2 with cyclooctene failed[38].

3. Insertion into metal-halogen bonds

Germylenes insert readily into many metal-halogen bonds to give polymetal derivatives.

Trichlorogermane etherate was found to react on π-$C_5H_5(CO)_2FeCl$ in tetrahydrofuran to form the complex π-$C_5H_5(CO)_2FeGeCl_3$, presumably via the insertion of $GeCl_2$ generated from ether solution of $HGeCl_3$, into the Fe–Cl bond[108]. This hypothesis was confirmed by the fact that $GeCl_2 \cdot C_4H_8O_2$ reacted with π-$C_5H_5(CO)_2FeCl$ with the formation of the same complex π-$C_5H_5(CO)_2FeGeCl_3$ in almost quantitative yield[109]. Reaction of $GeCl_2 \cdot C_4H_8O_2$ with π-$C_5H_5(CO)_2FeI$ yielded four complexes: π-$C_5H_5(CO)_2FeGeCl_3$, π-$C_5H_5(CO)_2FeGeCl_2I$, π-$C_5H_5(CO)_2FeGeClI_2$ and π-$C_5H_5(CO)_2FeGeI_3$ as a result of the disproportionation of the insertion product π-$C_5H_5(CO)_2FeGeCl_2I$ formed initially[109].

(π-$C_3H_5PdCl)_2$ was decomposed by $GeCl_2$ and GeI_2 to give diallyl as well as π-$C_3H_5PdX \cdot PPh_3$ after addition of Ph_3P. Under similar conditions $SnCl_2$ inserted into the Pd–Cl bond[159].

Bulten and Noltes[35,81] showed that the thermal disproportionation of $Et_2ClGeGeClEt_2$ at 230–250° gave predominantly Et_2GeCl_2 and $Et_2ClGeGeEt_2GeClEt_2$. Under the same conditions $Et_3GeGeClEt_2$ disproportionated with formation of Et_3GeCl and $Et_3Ge(GeEt_2)_nGeClEt_2$ (n = 1 or 2). The reaction mechanism involves the formation and subsequent insertion of a divalent germanium species:

$$Et_3GeGeClEt_2 \rightarrow Et_3GeCl + Et_2Ge$$

$$Et_2Ge + Et_3GeGeClEt_2 \rightarrow Et_3GeGeEt_2GeClEt_2$$

Insertion of diethylgermylene into the Ge–Cl bond seems highly plausible in view of the following results: thermolysis of a 1/1 mixture of $Et_3GeGeClEt_2$ and Me_3GeCl gives $Me_3GeGeClEt_2$ in addition to Et_3GeCl and $Et_3GeGeEt_2GeClEt_2$[35,81]

$$Me_3GeCl \xrightarrow{Et_2Ge} Me_3GeGeClEt_2 \xrightarrow{Et_2Ge} Me_3GeGeEt_2GeClEt_2$$

The insertion of germanium dichloride into $GeCl_4$ at 120° gave an equilibrium mixture in which the digermane $Cl_3GeGeCl_3$ was characterized[38]:

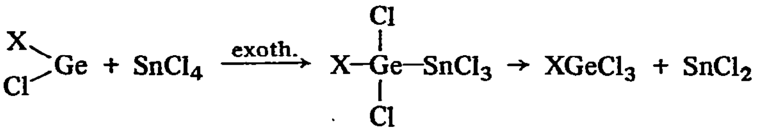
$$GeCl_2 + GeCl_4 \rightarrow Cl_3GeGeCl_3 \xrightarrow{EtMgBr}$$

$$Et_3GeGeEt_3(\text{traces}) + Et_4Ge + Et_3GeH + (Et_2Ge)_n$$

A very exothermic reaction took place when $GeCl_2$ was mixed with $SiCl_4$ and the transistory formation of the germa-silane $Cl_3GeSiCl_3$ can be postulated. However, its decomposition must have proceeded only by α-elimination on germanium, since only $SiCl_4$ is isolated upon fractionated distillation[38]:

$$GeCl_2 + SiCl_4 \rightarrow [Cl_3GeSiCl_3] \begin{cases} \nrightarrow GeCl_4 + SiCl_2 \\ \rightarrow (GeCl_2)_n + SiCl_4 \end{cases}$$

On the other hand, silicon tetrachloride as well as trialkylchlorosilanes were found to be inert toward ethylchlorogermylene at 160°. The reaction of $GeCl_2$ and EtGeCl with tin tetrachloride was totally different, being accompanied by decomposition of the initially formed germa-stannane with precipitation of stannous chloride:



(X = Cl, Et)

Moreover, several attempts to obtain the stannylene, BuSnCl, by exchange between $\mathrm{GeCl_2}$ and $\mathrm{BuSnCl_3}$ resulted in precipitation of $\mathrm{SnCl_2}$ in addition to the formation of $\mathrm{BuSnCl_3}$, $\mathrm{GeCl_4}$ and $\mathrm{BuGeCl_3}$[38].

It was shown that germanium dibromide inserts into the Ge-Br bond of germanium tetrabromide to give hexabromodigermane in a reversible reaction[42]:

$$\mathrm{GeBr_2 + GeBr_4 \rightleftarrows Br_3GeGeBr_3}$$

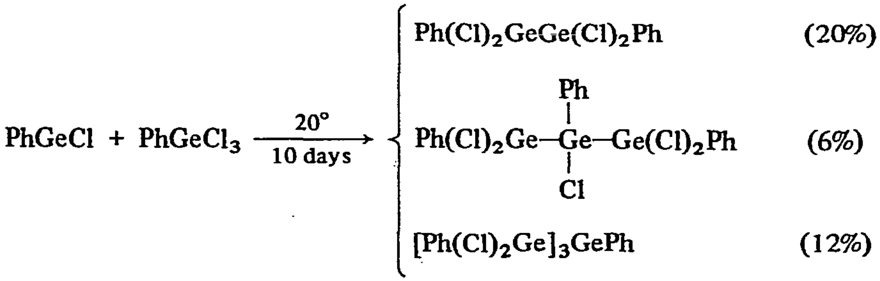
On the other hand, the dibromide failed to react with germanium tetrachloride and methylbromogermanes $\mathrm{(CH_3)_nGeBr_{4-n}}$[42].

We already reported (*cf.* II A) that the insertions of ethyl- and phenylchlorogermylenes, EtGeCl and PhGeCl, into the germanium-halogen bonds of the tetrahalides, $\mathrm{GeX_4}$ (X = Cl, Br, I), led to unstable organopentahalodigermanes. The decomposition of the latter gave $\mathrm{GeX_2}$ in a state of high purity[38,39,58]:

$$\mathrm{RGeCl + GeX_4 \xrightarrow{20^\circ} R(Cl)XGeGeX_3 \xrightarrow{20^\circ} R(X)_2GeCl + GeX_2}$$

(R = Et, Ph; X = Cl, Br, I)

Phenylhalogermylenes (PhGeX) (X = Cl, Br) inserted into the germanium-halogen bonds of various phenylhalogermanes to give phenylhalopolygermanes[39,37,58]:



$$\mathrm{PhGeCl + PhGeCl_3 \xrightarrow[10\ days]{20^\circ}} \begin{cases} \mathrm{Ph(Cl)_2GeGe(Cl)_2Ph} & (20\%) \\ \mathrm{Ph(Cl)_2Ge{-}\overset{Ph}{\underset{Cl}{Ge}}{-}Ge(Cl)_2Ph} & (6\%) \\ \mathrm{[Ph(Cl)_2Ge]_3GePh} & (12\%) \end{cases}$$

The di- and poly-germanes thus formed were characterized by their methylation with MeMgI to the respective phenylmethylpolygermanes.

In the mechanism of formation of polygermanes, the hypothesis of an insertion of germylene in the Ge–Ge bond must be excluded because the attempted insertion of phenylchlorogermylene into $\mathrm{Ph(Me)_2GeGe(Me)_2Ph}$ did not occur[39,58]. The insertion of phenylchlorogermylene into the Ge-Br bond of $PhGeBr_3$ was far more readily achieved and the equilibrium was displaced in favor of the polygermanes:

$$PhGeCl + PhGeBr_3 \xrightleftharpoons[12\,h]{20^\circ} Ph(Cl)(Br)GeGe(Br)_2Ph + [Ph(Cl)(Br)Ge]_2Ge(Br)Ph$$
$$\text{(Rdt. 80\%)}$$

The action of three moles of PhGeCl on one mole of $PhGeBr_3$ gave the digermane (26%), trigermane (15%) and the tetragermane (59%) $[Ph(Cl)(Br)Ge]_3GePh$[39,58]. However, the insertion of phenylbromogermylene into $PhGeBr_3$ took place in only low yields and did not proceed past the trigermane step:

$$PhGeBr + PhGeBr_3 \xrightleftharpoons{20^\circ} Ph(Br)_2GeGe(Br)_2Ph + [Ph(Br)_2Ge]_2GeBrPh$$

This very likely is due to the low stability of phenylbromogermylene and its strong tendency to polymerize.

The isolation of unsymmetrical polygermanes such as $Et_3GeGe(Cl)_2Ph$ and $Ph_2(Cl)GeGe(Cl)_2Ph$ from addition reactions of phenylchlorogermylene with Et_3GeCl and Ph_2GeCl_2, respectively, proved to be impossible owing to the high instability of such digermanes[39,58]:

$$Et_3GeCl + PhGeCl \;\overset{\not\longrightarrow}{\longleftarrow}\; Et_3GeGe(Cl)_2Ph$$

However, when the polygermane formed decomposes in a manner which does not regenerate the starting materials, *i.e.*, when there is no reversibility of the reaction, the insertion process can be demonstrated after methylation of the intermediate digermane[39,58]:

$$\begin{tikzcd}
PhGeCl + Ph_2GeBr_2 \arrow[r] & Ph(Cl)(Br)GeGe(Br)Ph_2 \arrow[r] \arrow[d, "MeMgI"] & (PhGeBr)_n + Ph_2(Cl)GeBr \\
 & Ph(Me)_2GeGe(Me)Ph_2 &
\end{tikzcd}$$

The insertion of phenylchlorogermylene into the germanium-chlorine bond of phenylchlorogermane led to 1,2-diphenyl-1,1-dichlorodigermane (17%). This reaction was accompanied by insertion of germylene into the Ge-H bond of the phenylchlorogermane[63,58]:

$$\begin{tikzcd}
 & Ph(Cl)_2GeGe(H)_2Ph\ (17\%)\ \text{(insertion into Ge-Cl)} \arrow[dl, shift left] \\
PhGeCl + Ph(Cl)GeH_2 \arrow[ur, shift left] \arrow[dr] & \\
 & Ph(Cl)(H)GeGe(H)(Cl)Ph\ (4\%)\ \text{(insertion into Ge-H)} \arrow[d] \\
 & Ph(Cl)_2GeH + (PhGeH)_n
\end{tikzcd}$$

4. Insertion into metal-hydrogen bonds

The germylene GeH_2 has been reported to be an intermediate species, especially in the insertion reaction into the silicon-hydrogen and germanium-hydrogen bonds. Pyrolysis of digermane at 230–240° gave germane and trigermane which could be interpreted in accordance with the following equations[87]:

$$Ge_2H_6 \rightarrow GeH_2 + GeH_4$$

$$GeH_2 + Ge_2H_6 \rightarrow Ge_3H_8$$

The products from the copyrolysis, at 280°, of digermane and deuterated ethylgermane, $EtGeD_3$, were germane, trigermane and ethyldigermane $CH_3CH_2Ge_2H_2D_3$, while diethyldigermanes were not observed. These results strongly suggest that digermane decomposes into germylene and germane; the germylene, GeH_2, then undergoes germanium-hydrogen bond insertion, leading to the observed products[87].

Germylene has been proposed as the species responsible for the formation of mixed silicon-germanium hydrides in the copyrolysis of silane and germane[110]. Fast neutron irradiation of a 1/1 germane-silane mixture (1/1 GeH_4-SiH_4) produced $H_3{}^{75}GeSiH_3$ as well as $^{75}GeH_4$ and $H_3{}^{75}GeGeH_3$. These reactions seem to involve the germylene radical $:{}^{75}GeH_2$ as a reactional intermediate[111]:

$$:{}^{75}GeH_2 + GeH_4 \rightarrow H_3{}^{75}GeGeH_3$$

$$:{}^{75}GeH_2 + GeH_4 \rightarrow {}^{75}GeH_4$$

$$:{}^{75}GeH_2 + SiH_4 \rightarrow H_3{}^{75}GeSiH_3$$

Alkyl- and phenylgermylenes, RGeH and PhGeH, have been allowed to react *in situ* with $EtGeH_3$ and $PhGeH_3$. In both cases the respective tetrahydrodigermane was obtained by insertion of germylene into the Ge-H bond[7,58]:

$$RGeH + RGeH_3 \rightarrow R(H)_2GeGe(H)_2R \quad \text{(15–20\% yield)}$$

Phenylchlorogermylene inserted simultaneously into the Ge-Cl bond and the Ge-H bonds of phenylchlorogermane with formation of 1,2-diphenyl-1,2-dichlorodigermane, Ph(Cl)(H)GeGe(H)(Cl)Ph[58,63].

The reaction of the phenylgermane, $PhGeH_3$, with the phenylchlorogermylene PhGeCl, gave 1,2-diphenyl-1-chlorodigermane stemming from an insertion of germylene into a Ge-H bond of the germane. This rather unstable digermane decomposed into $(PhGeH)_n$ polymer and phenylchlorogermane which underwent other phenylchlorogermylenes insertions into its Ge-H or Ge-Cl bonds[58,63]:

$$\begin{tikzcd}
PhGeH_3 + PhGeCl \arrow[r] & Ph(Cl)(H)GeGe(H)_2Ph \arrow[d] & \\
 & Ph(Cl)GeH_2 + (PhGeH)_n \arrow[d, "PhGeCl"] & \\
 & \arrow[dl, "\text{insertion into Ge-H}"'] \arrow[dr, "\text{insertion into Ge-Cl}"] & \\
Ph(Cl)(H)GeGe(H)(Cl)Ph & & Ph(Cl)_2GeGe(H)_2Ph
\end{tikzcd}$$

5. *Insertions into metal-carbon bonds*

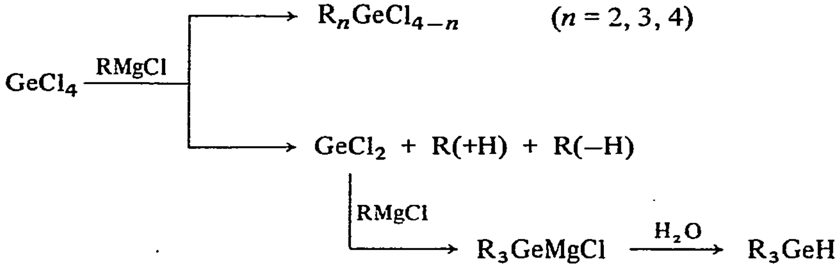
The action of Grignard reagents or organolithium derivatives on halogenated germylenes, GeX_2, usually leads to polymers $[R_2Ge]_n$, telomers $R[GeR_2]_nR$ or cyclopolymers $\boxed{[R_2Ge]_n}$ [22–24], but in certain cases the formation of intermediates such as R_3GeMgX or R_3GeLi can be postulated, which formally corresponds to the insertion of germylenes into the metal-carbon bond of the organometallic derivatives.

The formation of telomers can also be explained by the formation of intermediates of the type $R[GeR_2]_nMgX$.

Seyferth explained the formation of hexavinyldigermane by the action of vinylmagnesium bromide on germanium tetrachloride by the formation of transient $(CH_2{=}CH)_3GeMgBr$ which can be generated from germanium dichloride[112]:

$$GeCl_4 + 2RMgX \rightarrow GeCl_2 + R{-}R + 2MgXCl$$
$$GeCl_2 + 2RMgX \rightarrow GeR_2 + 2MgXCl$$
$$GeR_2 + RMgX \rightarrow R_3GeMgX$$
$$R_3GeMX + R_3GeCl \rightarrow R_3GeGeR_3$$

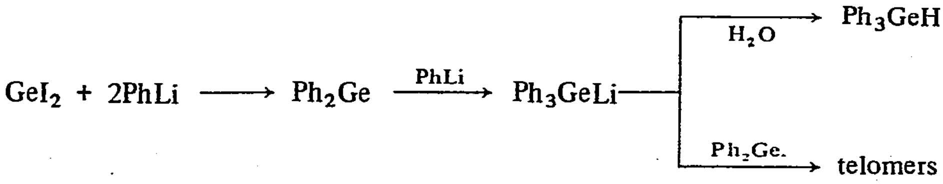
This reaction scheme allowed interpretation of the results of Mendelsohn, Valade *et al.* on the action of the hindered Grignard reagents on germanium tetrachloride which led to a high percentage of trialkylgermane[113,114]:



$(R = i\text{-}C_3H_7, C_5H_9, C_6H_{11})$

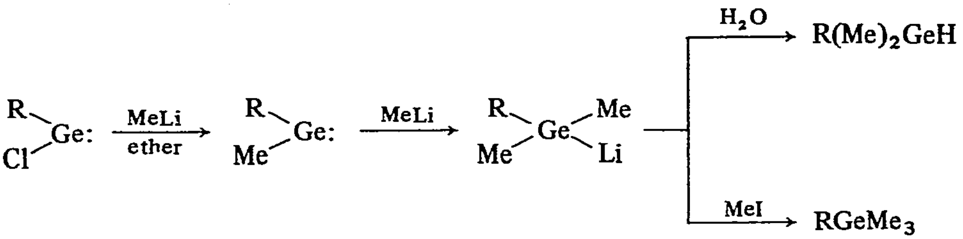
This mechanism was confirmed by the direct reaction of $C_6H_{11}MgCl$ with $GeCl_2$ which gave tricyclohexylgermane $(C_6H_{11})_3GeH$.

In the action of an excess of phenyllithium on GeI_2, Glockling and Hooton observed the presence of triphenylgermane after hydrolysis[75]:



A reaction of the same type has been observed in the action of mesitylmagnesium bromide on GeI_2.

The action of methyllithium on RGeCl (R = Et or Ph) which gave dimethylethyl- or -phenyl-germane after hydrolysis or to ethyl- or phenyl-trimethylgermane after treatment with methyl iodide (in addition to large quantities of telomers) can be interpreted in terms of the intermediate formation of a lithium germanium derivative[7]:

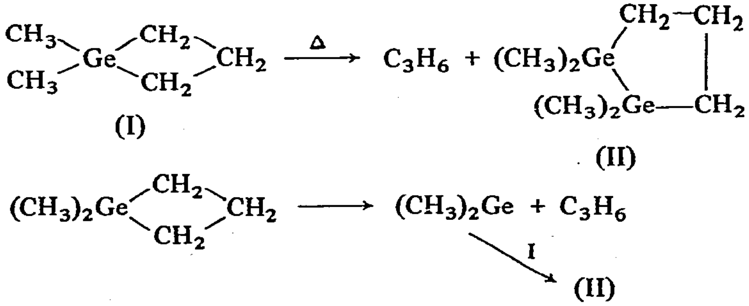


In the same way, the action of MeMgI on PhGeCl which gave after hydrolysis, $Ph(Me)_2GeH$ and polymers $(PhGeMe)_n$, can be rationalized in terms of an intermediate with a Ge-Mg bond[39,58]:

$$PhGeCl + 2MeMgI \rightarrow Ph(Me)_2GeMgI \xrightarrow{H_2O} Ph(Me)_2GeH$$

The insertion of $GeCl_2$ into the iron-carbon σ bond of the complex $\pi\text{-}C_5H_5(CO)_2FeCH_3$ with formation of $\pi\text{-}C_5H_5(CO)_2FeGeCl_2CH_3$ has been described[115]. In a further development, the same authors studied insertion of $GeCl_2$ into complexes of the general type $\pi\text{-}C_5H_5(CO)_2FeR$ and $\pi\text{-}C_5H_5(CO)_2FeCOR'$. The formation of complexes of type $\pi\text{-}C_5H_5(CO)_2FeGeCl_2R$ was observed when R = alkyl. The insertion of $GeCl_2$ into the Fe–C bond did not occur when the substituent R is strongly (C_6F_5, $COCF_3$, $COCH_3$) or even weakly (C_6H_5) electron attracting. The reactivity of the Fe–R bond toward $GeCl_2$ increased in the following series: $R = C_6H_5CH_2 < CH_3 < C_2H_5 < n\text{-}C_3H_7 < i\text{-}C_3H_7$. This series of reactivities of $\pi\text{-}C_5H_5(CO)_2FeR$ is in accord with the electrophilic nature of the complex $GeCl_2 \cdot C_4H_8O_2$ and $GeCl_2 \cdot C_4H_8O$, the attack of which on the Fe–R bond is faster with increasing electron density at the transition metal atom[116].

Nametkin *et al.*[117] described the first insertion of germylene into a germanium–carbon bond. The formation of 1,1,2,2-tetramethyl-1,2-digermacyclopentane during pyrolysis of 1,1-dimethyl-1-germacyclobutane can be explained by insertion of dimethylgermylene formed in the pyrolysis into the endocyclic Ge–C bond of the four-membered ring:



6. *Insertions into metal-metal bonds*

Some insertion reactions of germylenes into metal-metal bonds have been described in the literature.

Nesmeyanov *et al.*[108,118] observed insertion of $GeCl_2$ into the Fe-Fe bond of the dimer of π-cyclopentadienyliron dicarbonyl:

$$[\pi\text{-}C_5H_5Fe(CO)_2]_2 + C_4H_8O_2 \cdot GeCl_2 \rightarrow [\pi\text{-}C_5H_5Fe(CO)_2]_2GeCl_2$$

The same reaction with GeI_2 gave the iodine analog, $[\pi\text{-}C_5H_5Fe(CO)_2]_2GeI_2$ (76% yield)[119]. This latter compound is also prepared by action of GeI_2 in refluxing C_6H_6 on $[\pi\text{-}C_5H_5Fe(CO)_2]_2Hg$ (yield 21%)[158]. GeI_2 reacts also with $[\pi\text{-}C_5H_5M(CO)_3]_2Hg$ (M = Mo, W) to give the corresponding $[\pi\text{-}C_5H_5M(CO)_3]GeI_2$ in 10 and 22% yield, respectively[158].

Germanium diiodide reacted with dicobaltoctacarbonyl to form the Co-Co bond insertion product[120]:

$$Co_2(CO)_8 + GeI_2 \xrightarrow[THF]{20°} [Co(CO)_4]_2GeI_2$$

The anions $Cr_2(CO)_{10}^{2-}$ and $W_2(CO)_{10}^{2-}$ also have been found to react with GeI_2 to produce products of the type $[(CO)_5MGeI_2M(CO)_5]^{2-}$ (M = Cr, W)[121]. In the reaction of triphenylgermyllithium with GeI_2, which after hydrolysis gave $(Ph_3Ge)_3GeH$, the insertion of the germylene $(Ph_3Ge)_2Ge$ into the Ge-Li bond of Ph_3GeLi can be considered[75]:

$$2Ph_3GeLi + GeI_2 \rightarrow (Ph_3Ge)_2Ge \xrightarrow{Ph_3GeLi} (Ph_3Ge)_3GeLi \xrightarrow{H_2O} (Ph_3Ge)_3GeH$$

A reaction of the same type was observed between GeI_2 and the triethylgermyllithium in HMPT[35,97]:

$$2Et_3GeLi + GeI_2 \rightarrow (Et_3Ge)_2Ge \xrightarrow{Et_3GeLi} (Et_3Ge)_3GeLi \xrightarrow{MeLi} (Et_3Ge)_3GeMe$$

Treatment of (3)-1,2-$B_9C_2H_{11}^{2-}$ with divalent germanium (GeI_2), tin or lead species led to the formation of 1-germa- (1-stanna- or 1-plumba-) 2,3-dicarba-closo-dodecaborane (M = Ge, Sn, Pb)[122]. (Structure, see Fig. 1.)

Attempts to insert Et_2Ge in Ge-Ge bond of $Et_3GeGeEt_3$[35,81] or PhGeCl in Ge-Ge bond of $PhMe_2GeGeMe_2Ph$[39] have failed.

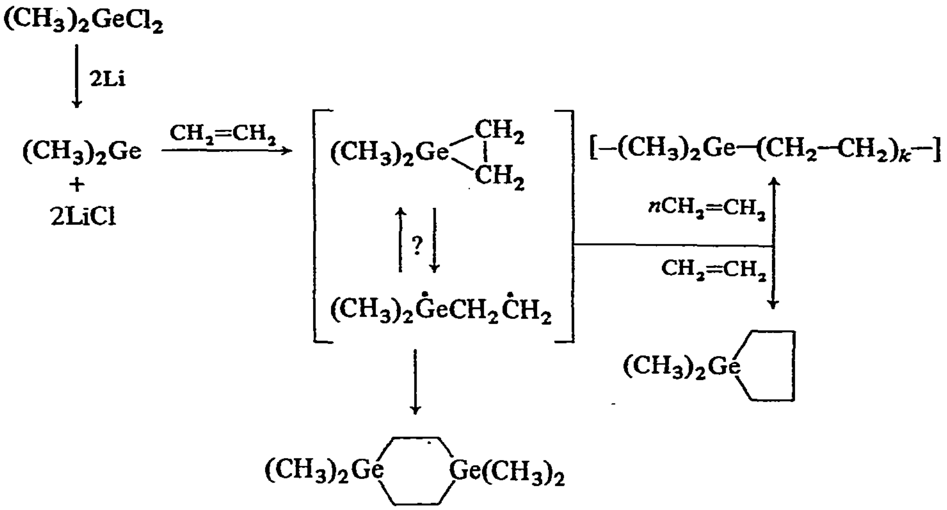
B. *Additions to carbon-carbon multiple bonds*

The first addition reactions of germylenes to nonconjugated (alkenes, alkynes) or conjugated (dienes) unsaturated systems were observed with the etherates of trihalogermanes. As already mentioned, these etherates are a source of dihalogermylenes.

But reactions of the pure divalent species such as $GeCl_2$, $GeCl_2 \cdot C_4H_8O_2$, $GeBr_2$, GeI_2, RGeX, as well as the dialkylgermylenes generated from R_2GeCl_2 in the presence of alkali metals, show identical addition reactions with the same unsaturated systems.

1. *Alkenes*

When dimethyldichlorogermane was treated with lithium in THF at 0–10° and ethylene passed through the reaction mixture, the products formed suggested the formation of dimethylgermylene, $(CH_3)_2Ge$[65,66]:



Reactions of the same type were observed when dimethyldichlorogermane reacted with alkali metals in the presence of arylethylenes such as styrene and vinyltoluene[64,66]. The reactions of trichlorogermane etherate with ethylene in a –30° to +40° temperature range gave organogermanium polymers of the general formula $[CH_2{-}CH_2{-}GeCl_2]_n$ (yields 50%) and a mixture of $Cl_2(H)GeCH_2CH_2GeCl_3$ and $Cl_3GeCH_2CH_2GeCl_3$. This reaction of $GeCl_2$ may be rationalized in terms of initial formation of an unstable three-membered heterocycle which polymerized partially. The formation of the pentachloride can be interpreted

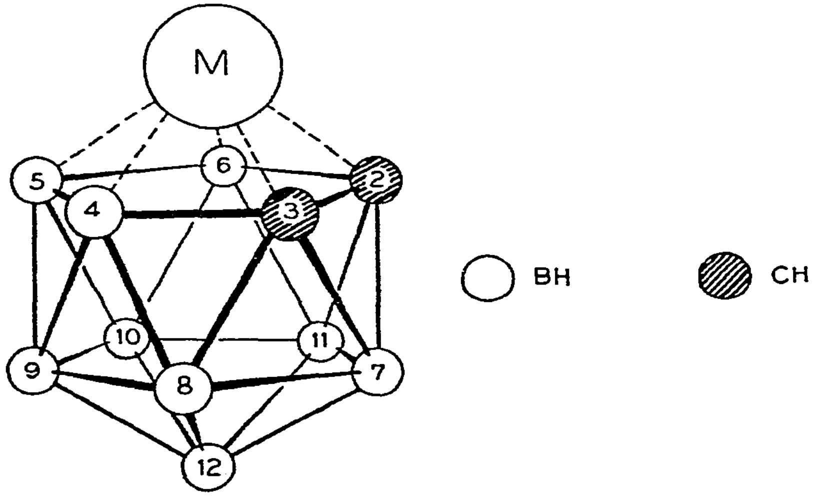
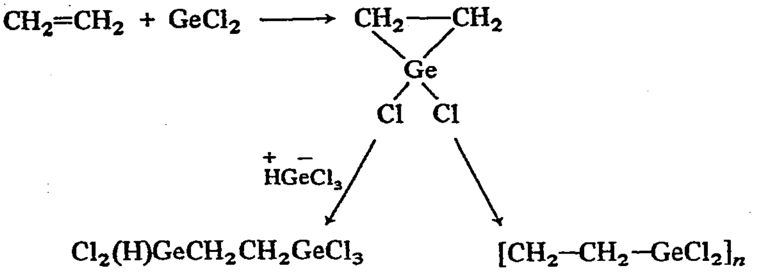


Fig. 1. Proposed structure and numbering convention for $MC_2B_9H_{11}$ compounds (M = Ge, Sn, Pb)[122].

by ionic addition of trichlorogermane to the unstable three-membered germacyclopropane[22,23,123,124]:



The action of trichlorogermane on allyl alcohol resulted in formation of polymers of the type $[Cl_2GeCH_2{-}\underset{\displaystyle CH_2OH}{\underset{|}{CH}}]_n$[125]. The $GeCl_2 \cdot$dioxane complex also give characteristic "carbene" reactions[28]. Interaction of $GeCl_2 \cdot C_4H_8O_2$ with olefins led to oligomeric and polymeric products with $GeCl_2$ groups in the main chain[30]. For example, reactions with $CH_2{=}CH{-}Cl$ and $CH_2{=}CCl_2$ gave exclusively polymers of the structure $[(CH_2CHR)_kGeCl_2]_n$, where $R = H$ or Cl and $k \approx 2$[31].

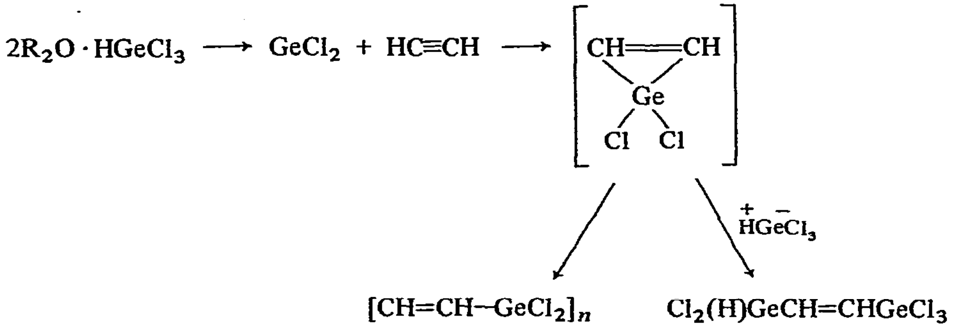
GeI_2 formed a polymer $[CH_2CH_2GeI_2]_n$, with $CH_2{=}CH_2$ (from decomposition of ICH_2CH_2I in a sealed tube at 150°)[106].

In the reaction of RGeCl and $GeCl_2$ with allyl chloride at normal temperature, polymers of type $[CH(CH_2Cl)CH_2Ge(Cl)R]_n$ (R = Et, Ph or Cl) were the major product[36].

On the other hand, attempts to trap diethylgermylene with carbon-carbon unsaturated systems such as tetracyanoethylene, 1-(diethylamino)cyclohexene or diphenylacetylene were unsuccessful[35,81].

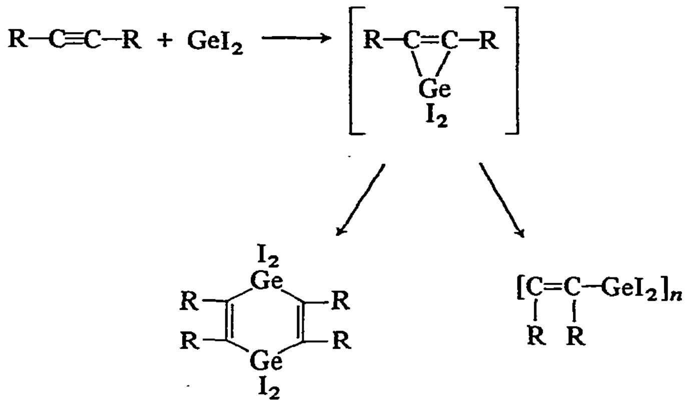
2. Alkynes

The addition of germylenes to acetylenic derivatives usually led, via formation of unstable germacyclopropenes, either to dimers or to polymers. With trichlorogermane etherates the reactions were analogous to those observed with ethylene[22,23,124,126,127].



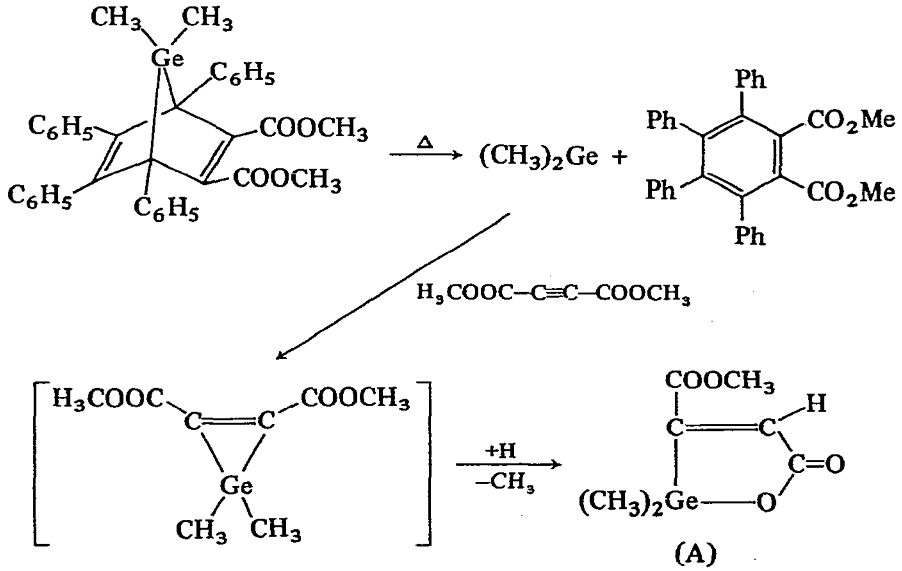
$HGeBr_3$, a source of $GeBr_2$, reacted with acetylene to give only a polymer of structure $[CH{=}CH{-}GeBr_2]_n$[41]. GeI_2 added to the C≡C bond of acetylene and diphenylacetylene. Vol'pin *et al.* had at first considered the formation of stable germacyclopropenes[128].

However, such germacyclopropenes, which probably were formed in a first step, actually were not stable, and the products isolated were digermacyclohexadienes and polymers[129,130,131,132]. Mass spectra[129,130] and X-ray analysis[131,132] gave evidence for the structure of these digermacyclohexadienes.



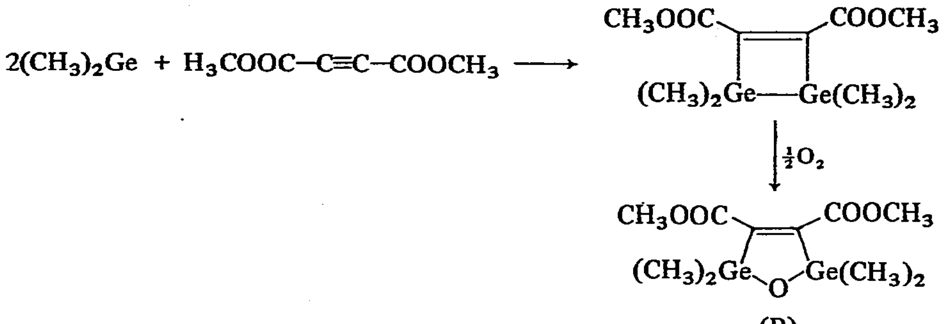
A similar reaction has been observed recently in the action of germanium diiodide and 2-butyne, leading to the corresponding 1,4-digerma-2,5-cyclohexadiene (yield: 30–40%)[156]

Pyrolysis of 2,3-dicarbomethoxy-7,7-dimethyl-1,4,5,6-tetraphenyl-7-germanorbornadiene gave dimethylgermylene which was characterized by means of its interception by dimethyl acetylenedicarboxylate[82]:



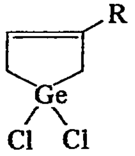
(A)

Besides the germa-γ-butyrolactone, (A), the formation of a second heterocycle, (B), was noted. The latter may have come from the condensation of two dimethylgermylene molecules to the acetylene, followed by the oxidation of the intermediate digermacyclobutene[82]:



3. Conjugated dienes and trienes

Trichlorogermane reacted with butadiene and isoprene at low temperature with formation of the 1,4 linear adduct, $Cl_3GeCH_2C(R){=}CH{-}CH_3$ ($R = H, CH_3$), and dichlorogermacyclopentene derivatives, (C), ($R = H, CH_3$), the 1,4 adducts of $GeCl_2$ (due to the dissociation of $HGeCl_3$)[127,133,134]. Nefedov *et al.* confirmed these results and noted that in the presence of an excess of butadiene, oligomers, $H[CH_2CH{=}CH{-}CH_2GeCl_2]_2Cl$, as well as polymers $[CH_2CH{=}CH{-}CH_2GeCl_2]_n$, were formed[124,135].

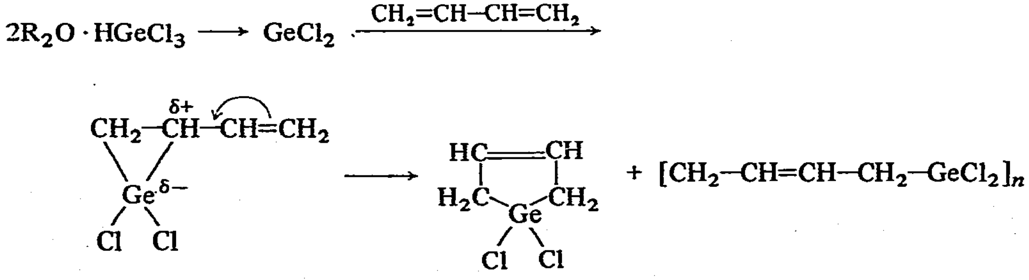


(C)

Trichlorogermane etherates reacted with gaseous butadiene at ≃ 20° in similar fashion.

Recently the 1,1-dichlorogerma-3-cyclopentene was obtained by treatment of germanium metal by a gaseous mixture of $GeCl_4$ and butadiene at 350–400° (yield 15%).

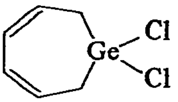
The formation of these compounds also probably results from the participation of $GeCl_2$, the first step being the 1,2-addition to butadiene to form an unstable, polarized three-membered heterocycle which then undergoes intramolecular ionic rearrangement to the stable five-membered ring:



However, an ionic mechanism giving the germacyclopentene directly is not excluded. When butadiene was bubbled through a solution of $GeCl_2 \cdot$ dioxane, polymer $[CH_2{-}CH{=}CH{-}CH_2{-}GeCl_2]_n$ and the cyclic monomer $\underline{CH_2{-}CH{=}CH{-}CH_2{-}GeCl_2}$ also were produced[28,30].

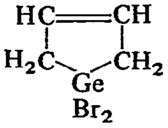
The interaction of the $GeCl_2 \cdot$ dioxane complex with 1,3,5-hexatriene gave 1,1-dichloro-1-germa-3,5-cycloheptadiene (yield 20–50%). This is the first example of a formal 1,5-cycloaddition of a carbene-like intermediate to a conjugated triene[30,136]:

$$C_4H_8O_2 \cdot GeCl_2 + CH_2{=}CH{-}CH{=}CH{-}CH{=}CH_2 \longrightarrow$$



$+ [GeCl_2C_6H_8]_n$

$GeBr_2$ reacted readily with butadiene, giving the cyclic compound, (D), exclusively (yield 28%)[41]:

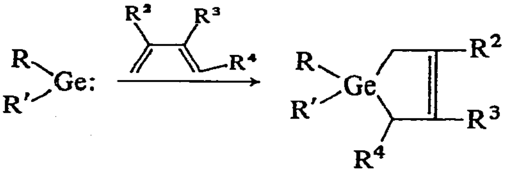


(D)

The yield of this product was 81% using $GeBr_2$ prepared according to the method of Curtis and Wolber[42].

The 1,4-addition of the germanium diiodide to butadiene, isoprene and 2,3-dimethyl-1,3-butadiene also led to diiodogermacyclopentene derivatives[97,137], but no reaction was observed with cyclopentadiene, 1,3-cyclooctadiene, piperylene, 1-phenyl-1,3-butadiene, tetraphenylbutadiene, 2,3-dichloro-1,3-butadiene and hexachlorocyclopentadiene[97]. In the absence of solvent (hexane), GeI_2 did not react with butadiene[97,128,134].

The addition of mixed germylenes (R)(R′)Ge (R = alkyl or phenyl) (R′ = F, Cl, Br, I, H or MeO) to conjugated dienes such as isoprene, 2,3-dimethyl-1,3-butadiene or 1,3-pentadiene allowed the preparation of the first 1-germa-3-cyclopentenes with different substituents on the germanium atom[7,57,58,138].



$R^2 = CH_3;\ R^3 = R^4 = H$
$R^2 = R^3 = CH_3;\ R^4 = H$
$R^2 = R^3 = H;\ R^4 = CH_3$

C. Other reactions of germylenes

1. Reactions with organometallic derivatives

Grignard reagents and organolithium derivatives have been allowed to react with different divalent Ge species (GeX_2, $RGeX$), as well as with trihalogermanes or their etherates or pyridine complexes. Polymers, $(R_2Ge)_n$, telomers $R[R_2Ge]_nR$ ($n \geqslant 2$), or cyclopolymers $\overline{(R_2Ge)}_n$ ($n = 4$) were characterized as products in these reactions[7,22,23,24,39,75,76]. The formation of germanium-metal intermediates, R_3GeMgX or R_3GeLi, by insertion of germylenes into metal-carbon bond (see section III A5) was believed to be an essential feature of these reactions.

Some other reactions between germylenes and organoaluminium, organozinc and organomercury derivative also have been described. Germanium diiodide and trimethylaluminium reacted at 20° in hexane to form noncyclic, branched-chain methylpolygermanes $Me_{2n+2}Ge_n$ ($n = 4$–10) and compounds resulting from the growth of alkyl chains (*e.g.* Me_9Ge_4Et and Me_9Ge_4Pr)[139–141]. Triethylaluminium reacted similarly, but also formed Et_6Ge_2 and Et_8Ge_3, while $i\text{-}Bu_3Al$ yielded the isobutyliodogermanes $i\text{-}BuGeI_3$, $i\text{-}Bu_5Ge_2I$ and $i\text{-}Bu_7Ge_3I$[141]. The reaction between GeI_2 and triphenylaluminium ether complex produced a yellow solid polymer containing residual iodine[75].

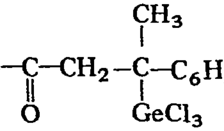
Jacobs reported the formation of $Bu_2IGeGeIBu_2$ in the reaction of Bu_2Hg with GeI_2[142]. A study was made by Emelyanova, Nesmeyanov *et al.*[143,144] of the reaction of germanium diiodide with numerous diarylmercury compounds. The main reaction products were diarylgermanium diiodides:

$$Ar_2Hg + GeI_2 \rightarrow Ar_2GeI_2 + Hg \quad \text{(40–75\% yield)}$$

In some cases, triarylgermanium iodides and also small amounts of monoarylgermanium compounds, $ArGeI_3$, were formed as well.

The action of Ph_3GeLi and Et_3GeLi on GeI_2 has been described in (section III A6). The reaction of dibutylzinc with germanium diiodide give polymers with molecular weight from 20 000 to 100 000, but the structure of these polymers was not given[142].

2. Reactions of germylenes with carbonyl compounds

The interaction of the dioxane-germanium dichloride complex with ketones resulted in crotonic condensation and led to the same product as did the reaction of such ketones with $HGeCl_3$[100,101,145,146]. In particular, the trichloride  $C_6H_5\text{—}C(=O)\text{—}CH_2\text{—}C(CH_3)(GeCl_3)\text{—}C_6H_5$ was obtained from acetophenone, while the reaction with acetone gave $Cl_3GeC(CH_3)_2CH_2\text{-}COCH_3$ which is also formed by the interaction of acetone with trichlorogermane[147].

Consequently, crotonic condensation of ketones occurs not only under the influence of $HGeCl_3$, but can also be promoted by germanium dichloride which possesses Lewis acid properties:

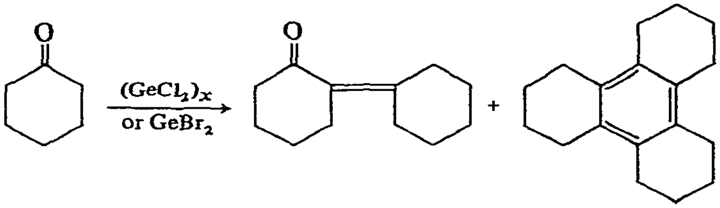
$$2(CH_3)_2CO \xrightarrow[HGeCl_3]{GeCl_2\text{ or}} (CH_3)_2C{=}CHCOCH_3 + H_2O$$

$$GeCl_2 + 2H_2O \rightarrow Ge(OH)_2 + 2HCl$$

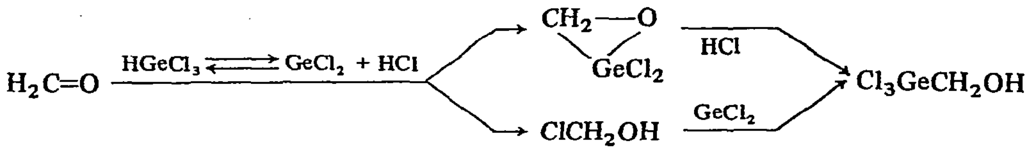
$$GeCl_2 + HCl \rightarrow HGeCl_3 \xrightarrow{(CH_3)_2C{=}CHCOCH_3} Cl_3GeC(CH_3)_2CH_2COCH_3$$

The same reaction, with formation of $Br_3GeC(CH_3)_2CH_2COCH_3$, was also observed with $GeBr_2$[42].

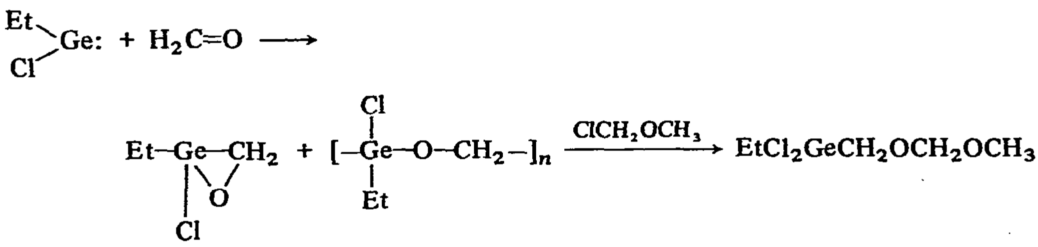
Uncomplexed germanium dihalides $(GeCl_2)_x$ and $GeBr_2$ also cause condensation of cyclohexanone and other ketones to the corresponding dimers and cyclic trimers. For example[101].



In the addition of $HGeCl_3$ to formaldehyde with formation of trichlorogermylmethanol: $HGeCl_3 + H_2C{=}O \rightarrow Cl_3GeCH_2OH$, other modes of reaction of $GeCl_2$ cannot be ruled out[148]:



In the action of EtGeCl on chloromethyl ether, the formation of a second derivative $EtCl_2GeCH_2OCH_2OCH_3$ besides the normal insertion product $EtCl_2GeCH_2COCH_3$, was observed. The presence of this derivative can be interpreted in terms of addition of the germylene to formaldehyde[36] (formed by thermolysis or acid hydrolysis of $ClCH_2OCH_3$):



3. Reducing properties of germylenes

One of the main chemical properties of the Group IVb divalent species R_2M is their tendency to undergo readily oxidation to the tetravalent state. Trichlorogermane, which dissociates into $GeCl_2$ and HCl, exhibits reducing properties. The reduction of various inorganic compounds by trichlorogermane has been reported (ref. 21 and 149 and literature cited).

Trichlorogermane and its etherates were found to reduce nitrobenzene and other aromatic nitro-compounds to the corresponding amines even at room temperature (yields 80–90%)[22,23,149]:

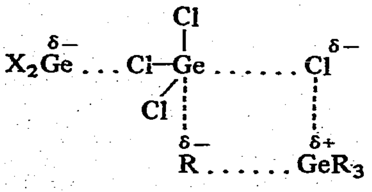
$$ArNO_2 \xrightarrow[CH_3ONa(CH_3OH)]{HGeCl_3 \text{ or } Et_2O, HGeCl_3} ArNH_2 + (CH_3O)_4Ge$$

Trichlorogermane and its etherates reduced $FeCl_3$ to $FeCl_2$ and ArN_3 to $ArNH_2$. The presence of other functional groups (*e.g.* halogen, sulfonyl group, carbon–carbon multiple bond, etc.) in the same molecule does not prevent almost quantitative selective conversion of the nitro group to an amino group[146]. The reducing power of $HGeCl_3$ and its etherates. analogous to the water and ether solution of $SnCl_2$ and HCl confirms the structure of these germanium compounds as associates of $GeCl_2$ and HCl and explains the tendency of trichlorogermane and especially of its etherates to generate germanium dichloride[149].

4. Lewis acid character (catalytic properties)

Germanium dichloride to a considerable degree resembles a Lewis acid. For example, $AlCl_3$ and $ZnCl_2$ with hydrogen chloride, give related compounds: $H^+(GeCl_3)^-$, $H^+(AlCl_4)^-$ or $H^+(ZnCl_3)^-$. This property of trichlorogermane and germanium dichloride is manifested in the ability of $(GeCl_2)_x$ to catalyze certain alkylation reactions, for example, the autocondensation of benzyl chloride[23,135,150].

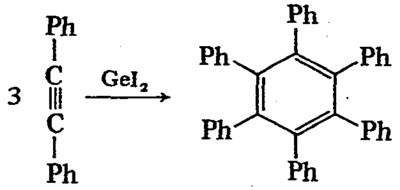
Transalkylation reactions between germanium derivatives as R_4Ge and $GeCl_4$, R_3GeGeR_3 and $GeCl_4$ have been found to be catalyzed by germanium diiodide and also by compounds containing a Ge–H function and by reducing agents such as $LiAlH_4$ and Raney nickel. It was assumed that in these reactions a germanium dihalide acts as the common catalytically active species and the germanium tetrachloride in the system is reduced to the bivalent state by the reducing agents cited, including the organogermanium hydrides[35,80,151]. The catalytic activity of a germanium dihalide in these reactions could be explained by assuming complex formation with germanium tetrachloride, resulting in a better stabilization of the transition state:



Chlorine–halogen exchange in phenylchlorogermane series are catalysed by GeI_2[158].

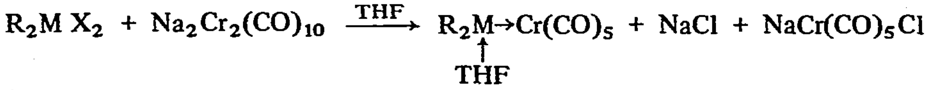
$$PhGeCl_3 + 2PhGeH_3 \xrightarrow[8\ h,\ 120°C]{GeI_2} 3Ph(Cl)GeH_2$$

GeI_2 catalyzes the trimerisation of diphenylacetylene[149]:



The reactions of secondary and tertiary phosphines with germanium diiodide which give compounds of the general formula $R_3P \cdot GeI_2$[153] are analogous to the reactions between phosphines and dihalocarbenes, which give phosphinedihalomethylene derivatives[1]; this fact suggests a carbene-like behavior of germanium(II) iodide.

The low temperature (–78°) reaction of $Na_2Cr_2(CO)_{10}$ in THF with dialkylgermanium and dialkyltin dihalides yielded pentacarbonylchromium complexes of dialkyl-germylenes and -stannylenes[154]:



$$R_2MX_2 + Na_2Cr_2(CO)_{10} \xrightarrow{THF} \underset{\substack{\uparrow \\ THF}}{R_2M} \rightarrow Cr(CO)_5 + NaCl + NaCr(CO)_5Cl$$

$(R = CH_3, M = Ge, Sn)$

The divalent metals appear to function simultaneously as Lewis acids (to THF) and strong Lewis bases (to chromium)*.

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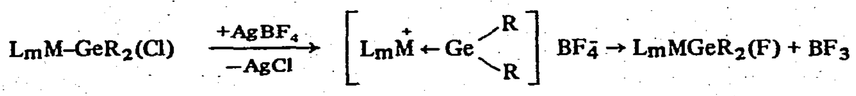
**Note added in proof.* The same behavior of Ge^{II} is postulated in the formation of a cationic transition metal complex of germylene during fluorination of chlorogermanium(IV) organo-transition metal compounds by silver tetrafluoroborate[161].



$$LmM\text{–}GeR_2(Cl) \xrightarrow[-AgCl]{+AgBF_4} \left[Lm\overset{+}{M} \leftarrow Ge\begin{smallmatrix} R \\ R \end{smallmatrix} \right] BF_4^- \rightarrow LmMGeR_2(F) + BF_3$$

(M = Mo, Fe, Co, Mn)

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