GERMANIUM

ANNUAL SURVEY COVERING THE YEAR 1973

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CONTENTS

Books and reviews

Apart from the Annual Survey covering the year 1971 (1), a review on the chemistry of organometallic compounds of Group IV elements has appeared (2). In a review article Satgé et al. discussed the synthesis and reactions of divalent species of germanium (e.g. dihalogermylenes, diorganogermylenes and germylene) and such species as starting materials and intermediates in organogermanium chemistry (3). The preparation and reactions of various radicals containing Group IVB elements have been reviewed (4). Few other general articles (5 - 8) which cover broad aspects of organogermanium chemistry have appeared.

Review articles on specific classes of compounds are included below under the relevant headings.

Direct syntheses and germanium-halogen compounds

Kocheshkov and coworkers extended their studies (see AS71; p. 126) on the direct synthesis of higher alkyltrihalogermanes (9):

$$RBr + Ge \xrightarrow[220^\circ\ ;\ 13\ hrs.]{sealed\ tube} RGeBr_3$$

$$\left[R = n\text{-}C_4H_9\ (51\%);\ n\text{-}C_6H_{13}\ (65\%);\ n\text{-}C_8H_{17}\ (55\%)\right]$$

and patented the method (10) involving the use of ionizing radiation ($^{60}Co\ \gamma$-rays):

$$n\text{-}C_4H_9Br + Ge \xrightarrow[sealed\ tube]{180 - 200^\circ\ ;\ 10 - 15\ hrs.} \underset{(54\%)}{n\text{-}C_4H_9GeBr_3}$$

The activities of the single phase Cu - Ge alloys in the reaction with methyl chloride to form methylchlorogermanes have been

measured at 426.7°C. Mechanical mixtures of alloys and free germanium showed greatly enhanced reactivities which could be explained only by the creation of additional reaction sites.
The X-Ray evidence has been presented indicating an initial increase in germanium concentration in thin surface layers of the alloy.
This has been attributed to the removal of copper by formation and sublimation of CuCl:

$$CH_3Cl + Cu \longrightarrow CH_3^{\cdot} + CuCl$$

This would provide a mechanism for the transport of copper (as CuCl) to the particles of germanium and the formation of deposits of copper on the surface of these particles. The peripheries of these deposits would then provide additional Cu – Ge sites for the formation of methylchlorogermanes (11, 12).

A number of organotriiodogermanes have been prepared by the reaction between germanium tetraiodide and organic iodides in the presence of zinc dust in an inert atmosphere (nitrogen or argon) (13):

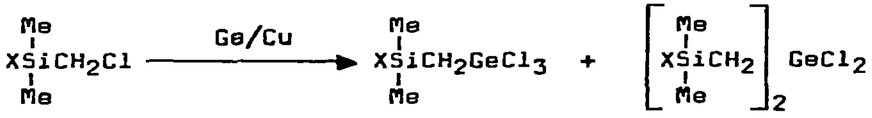
$$GeI_4 + RI \xrightarrow[5\ hrs.]{180 - 200^{\circ}} RGeI_3$$

$$\left[R = C_5H_{11}\ (48\%);\quad C_6H_{13}\ (52\%);\quad C_7H_{15}\ (55\%);\quad C_6H_5\ (53\%)\right]$$

Mironov et al. studied the reactions of germanium with gem- and α,ω-dihaloalkanes (15) and (chloromethyl) silanes (14, 15) with the object of extending the preparative possibilities of the 'direct synthesis' of organogermanium compounds. Some of their results are compiled in Chart 1.

$$X(CH_2)_nX \xrightarrow[370-380^\circ]{Ge/Cu} X(CH_2)_nGeX_3 + X_3Ge(CH_2)_nGeX_3$$

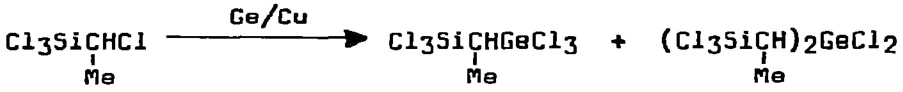
(X = Cl, Br; n = 1 - 5)



$$XSi(Me)_2CH_2Cl \xrightarrow{Ge/Cu} XSi(Me)_2CH_2GeCl_3 + [XSi(Me)_2CH_2]_2GeCl_2$$

(I) (II)

[X = F (I, 6%; II, 47%); OMe (I, 8%; II, 26%); OSiMe₃ (I, 5%; II, 41%)]



$$Cl_3SiCH(Me)Cl \xrightarrow{Ge/Cu} Cl_3SiCH(Me)GeCl_3 + (Cl_3SiCH(Me))_2GeCl_2$$

(32%) (12%)

$$Cl_nMe_{3-n}SiCH_2Cl \xrightarrow[370-400^\circ]{Ge/Cu} Cl_nMe_{3-n}SiCH_2GeCl_3 + (Cl_nMe_{3-n}SiCH_2)_2GeCl_2$$

(n = 0 - 3)

Chart 1. Direct synthesis of some organogermanium compounds.

The mechanism of insertion (see AS 72 ; p. 223) of $GeCl_2$: (generated from its dioxane complex) into carbon-chlorine bonds has been studied through an examination of its reaction with benzyl chlorides (16):

$$GeCl_2: + RC_6H_4CH_2Cl \longrightarrow RC_6H_4CH_2GeCl_3$$

(R = p-Me, H, p-Br, p-Cl, m-CF_3; yield: 80 - 95%)

The rate of insertion decreased in the stated order of R.

The method of preparation of phenyltrichlorogermanes of the type $Cl_nC_6H_{5-n}GeCl_3$ (n = 1 - 3)by direct chlorination of phenyltrichlorogermane at 70 - 75° in the presence of a catalyst (e.g. $FeCl_3$) has been patented (17).

Alkylation and arylation

Curtis and Scibelli reported the synthesis of bis(π-cyclopentadienyl)germanium (germanocene) according to the reaction (18, 19):

$$GeBr_2 + 2C_5H_5Na \xrightarrow[Et_2O]{-70^o} \underset{(60\%)}{(C_5H_5)_2Ge} + 2NaBr$$

The polymerization of solid germanocene has been shown to occur much more rapidly than that of stannocene. Aside from its high reactivity toward oxygen and its tendency to polymerize, germanocene is surprisingly unreactive compared to the germanium dihalides and other carbenoids. The lack of carbenoid reactivity has been attributed to π-bonding between the cyclopentadienyl rings and germanium. Striking spectral similarities between germanocene and π-bonded metallocenes are observed.

The preparation and properties of the cyclopentadienyl, indenyl and fluorenyl derivatives of Group IVB elements have been reviewed (20).

The synthesis of tetra-1-adamantylgermane (21) and tetraneopentylgermane (22) has been accomplished either by using the appropriate organolithium reagent or via a Wurtz-Fittig type reaction:

$$GeCl_4 + 4C_{10}H_{15}Br \xrightarrow[\text{cyclohexane}]{\text{Na; reflux}} (C_{10}H_{15})_4Ge \quad (26\%)$$

$$GeCl_4 + 4Me_3CCH_2Li \xrightarrow[-LiCl]{n\text{-hexane}} (Me_3CCH_2)_4Ge + (Me_3CCH_2)_3GeCl$$

The alkylation or arylation of germanium tetrahalides could be achieved according to the reaction (13, 23):

$$GeI_4 + RI + Zn \xrightarrow[\text{inert atmos.}]{160 - 200^\circ} R_4Ge$$

[R = Bu (85%); Ph (52%)]

The chemistry of polyfluoroaromatic (24) and fluoroalicyclic (25) derivatives of metals and metalloids (including those of germanium) has been reviewed.

Germanium-hydrogen compounds

Nametkin and coworkers extended their investigations (see AS 72; p. 226) on the reduction of germanium tetrachloride by organosilicon hydrides in the presence of triethylamine (26). In the presence of equivalent amounts of triethylamine, the hydrogen-chlorine exchange has been shown to occur readily between germanium tetrachloride and silicon hydrides of the more varied compositions and structures giving almost quantitative yields of the complex $HGeCl_3.Et_3N$:

$$\begin{tikzcd} GeCl_4 + R^1R^2SiHCl + Et_3N \arrow[d, "0^\circ"', "\text{hydrocarbon solvent}"] \\ HGeCl_3.Et_3N + R^1R^2SiCl_2 \end{tikzcd}$$

(R^1 = alkyl, aryl, H; R^2 = Cl, alkyl, aryl)

The method seems to be a convenient route to trichlorogermane complexes which are excellent starting materials for a variety of organogermanium compounds.

A high yield synthesis of triiodogermane (characterized by Raman spectroscopy in liquid hydrogen iodide) has been accomplished according to the reaction (27):

$$GeI_2 + HI \rightleftharpoons HGeI_3$$

The pale yellow solution is stable below -50°, but decomposes at room temperature:

$$HGeI_3 + HI \longrightarrow GeI_4 + H_2$$

The authors also claim that in the reaction of stoichiometric amounts of hydrogen iodide with $GeBr_2$ or a $GeBr_4/GeI_2$ mixture there are formed, besides $HGeI_3$, the trihalides $HGeBrI_2$ and $HGeBr_2I$, which cannot be isolated but can be recognized from their Raman spectra.

The sealed-tube reactions of iodine with GeH_4 and GeD_4 have been shown to give H_3GeI and D_3GeI respectively (28).

Vyazankin et al. synthesized tris (pentafluorophenyl) germane via following reactions (29):

$$\begin{tikzcd}
(C_6F_5)_3GeBr + Et_3GeH \arrow[r, "\text{1 hr. reflux}", "\text{no solvent}"'] \arrow[d, "LiAlH_4"', "\begin{array}{l}Et_2O/PhMe\\ \text{room temp.}\end{array}"] & (C_6F_5)_3GeH + Et_3GeBr \\
(C_6F_5)_3GeH & (89.5\%) \\
(78.5\%) &
\end{tikzcd}$$

Unlike non-fluorinated organogermanes which may be readily brominated at the germanium-hydrogen bonds (30, 31), the above derivative only reacts with bromine under sufficiently drastic conditions:

$$(C_6F_5)_3GeH \; + \; Br_2 \xrightarrow[100^{\circ}\text{ ; 6 hrs.}]{\text{PhH ; under vac.}} \underset{(71\%)}{(C_6F_5)_3GeBr} \; + \; HBr$$

Some transition metal carbene complexes have been found to react with organo Group IV B hydrides in the presence of a coordinating base (pyridine, acetonitrile) (32, 33):

$$R_3MH \; + \; (CO)_5M^1C(X)C_6H_4Y \xrightarrow[\text{base}]{\text{hexane}} \underset{(46 - 82\%)}{R_3MCHXC_6H_4Y} \; + \; M^1(CO)_5.\text{base}$$

$$\left[\begin{array}{l} R \; = \; Et, Pr, Ph \text{ etc.}; \; M \; = \; Si, Ge, Sn; \; M^1 \; = \; Cr, Mo, W; \\ X \; = \; OMe, NC_nH_{2n} \; (n = 2, 4) \text{ and } Y \; = \; p\text{-}OMe, p\text{-}Me, H, p\text{-}Cl \end{array}\right]$$

A number of competition experiments using the reaction:

$$\begin{tikzcd}
R_3MH \; + \; Cr(CO)_5 \; [:C(OMe)Ph] \arrow[d, "\text{hexane}"', "C_5H_5N"] \\
R_3MCH(OMe)Ph \; + \; Cr(CO)_5.C_5H_5N \; + \; cis\text{-}Cr(CO)_4.2C_5H_5N
\end{tikzcd}$$

$$(R \; = \; Et, Pr, Ph \text{ etc.}; \; M \; = \; Si, Ge, Sn)$$

have been carried out to show that the susceptibility of R_3MH to insertion of the fragment $[:C(OMe)Ph]$ varies in the order:

$Et_3SiH > Ph_3SiH < Ph_3GeH < Ph_3SnH, Pr_3SnH$

Eaborn and Jenkins observed that triphenylgermane readily undergoes hydrogen-exchange (at the Ge – H bond) with alcohols in the presence of a base (34). The exchange probably arises from the reversible reaction:

$$Ph_3GeH + OR^- \rightleftharpoons Ph_3Ge^- + ROH$$

Germanium-metal compounds

Vyazankin and coworkers extended their studies on the preparation (see AS 72 ; p.228) and reactions of organogermyl-mercury derivatives containing pentafluorophenyl fragments (29, 35). These are summarized in Chart 2.

$$2(C_6F_5)_3GeH + R_2Hg \xrightarrow{PhMe} [(C_6F_5)_3Ge]_2Hg + 2RH$$

(50%)

$[R = Et, (Me_3Si)_2N]$

$$(C_6F_5)_3GeH + Et_2Hg \longrightarrow (C_6F_5)_3GeHgEt + EtH$$

(38%)

$$2(C_6F_5)_3GeH + (Et_3Ge)_2Hg \xrightarrow{140^\circ} [(C_6F_5)_3Ge]_2Hg + 2Et_3GeH$$

(40%)

$$2(C_6F_5)_3GeBr + (Et_3Ge)_2Hg \xrightarrow[PhH]{h\nu} [(C_6F_5)_3Ge]_2Hg + 2Et_3GeBr$$

(75%)

$$\begin{tikzcd}
{[(C_6F_5)_3Ge]_2Hg + HgCl_2} \arrow[r, "\text{THF}", "100^{\circ}\text{; 4 hrs.}"'] \arrow[d, "\text{PhMe}\ 60\text{ hrs.}"', "\text{UV}\ 50-60^{\circ}"] & 2(C_6F_5)_3GeHgCl \arrow[d] \\
{Hg + (C_6F_5)_3GeGe(C_6F_5)_3 + (C_6F_5)_3GeH + (C_6F_5)_3GeCH_2Ph} & 2(C_6F_5)_3GeCl + 2Hg
\end{tikzcd}$$

(94%) (52%) (32%) (24%)

$$[(C_6F_5)_3Ge]_2Hg + (Et_3Ge)_2Hg \xrightarrow[\text{PhH}]{20^{\circ}} 2(C_6F_5)_3GeHgGeEt_3$$

(89.5%)

$$\begin{tikzcd}
{(C_6F_5)_3GeHgGeEt_3 + (C_6F_5)_3SnBr} \arrow[d, "\text{PhMe, UV}\ 20^{\circ}\text{; 30 min.}"', "\text{evacuated Mo-glass tube}"] \\
{(C_6F_5)_3SnHgGe(C_6F_5)_3 + Et_3GeBr}
\end{tikzcd}$$

(47%) (87%)

$$\begin{tikzcd}
{(Et_3Ge)_2Hg + 2(C_6F_5)_3SnBr} \arrow[r, "20^{\circ}\text{; 1 hr.}"] \arrow[d, "20^{\circ}\text{; 1 hr.}"', "\text{PhMe ; UV}"] & {[(C_6F_5)_3Sn]_2 + 2Et_3GeBr + Hg} \\
{(C_6F_5)_3SnHgSn(C_6F_5)_3 + 2Et_3GeBr} &
\end{tikzcd}$$

(47%)

Chart 2. Synthesis and reactions of some organogermyl-mercury derivatives.

The preparation of 1-triethylgermylmercury derivatives of 1,2- and 1,7-dicarba-closo-dodecaborane [12] has been achieved via the reactions (36):

$$\begin{tikzcd}(Et_3Ge)_2Hg \;+\; Hg(C_2B_{10}H_{10}R)_2 \arrow[r] \arrow[d, "R^1HgC_2B_{10}H_{10}R"] & 2Et_3GeHgC_2B_{10}H_{10}R \\ Et_3GeHgC_2B_{10}H_{10}R \;+\; Et_3GeHgR^1 & \end{tikzcd}$$

$(R = H, Me, CH_2Cl, Ph ; R^1 = Cl, Me, Ph)$

A synthetic route to optically active bis(methyl-1-naphthylphenylgermyl) mercury involves the reaction (37):

$$2(+)\text{-}R_3Ge^{*}H \;+\; t\text{-}Bu_2Hg \xrightarrow[80^{o}\ ;\ 8\ hrs.]{hexane\ ;\ vac.} (-)\text{-}(R_3Ge^{*})_2Hg \;+\; 2t\text{-}BuH$$

$[R_3Ge^{*} = Me(1\text{-}C_{10}H_7)PhGe^{*}]$

The product has been shown to undergo an exchange reaction of the type:

$$\begin{aligned}(R_3Ge^{*})_2Hg \;+\; Hg(CH_2COOMe)_2 \xrightarrow[9\ days]{THF\ ;\ vac.}\; & 2(+)\text{-}R_3Ge^{*}CH_2COOMe \\ & +\ \underset{(87\%)}{2Hg}\ +\ \underset{(20\%)}{(R_3Ge^{*})_2O}\end{aligned}$$

The reactions of bis(triethylgermyl) cadmium with carbonyl compounds probably proceed through the intermediate formation of $>\dot{C}\text{-}O\text{-}GeEt_3$ radicals, which dimerize or withdraw hydrogen from the carbonyl-containing compound (38). Some of these reactions and others with compounds containing multiple bonds are given in Chart 3.

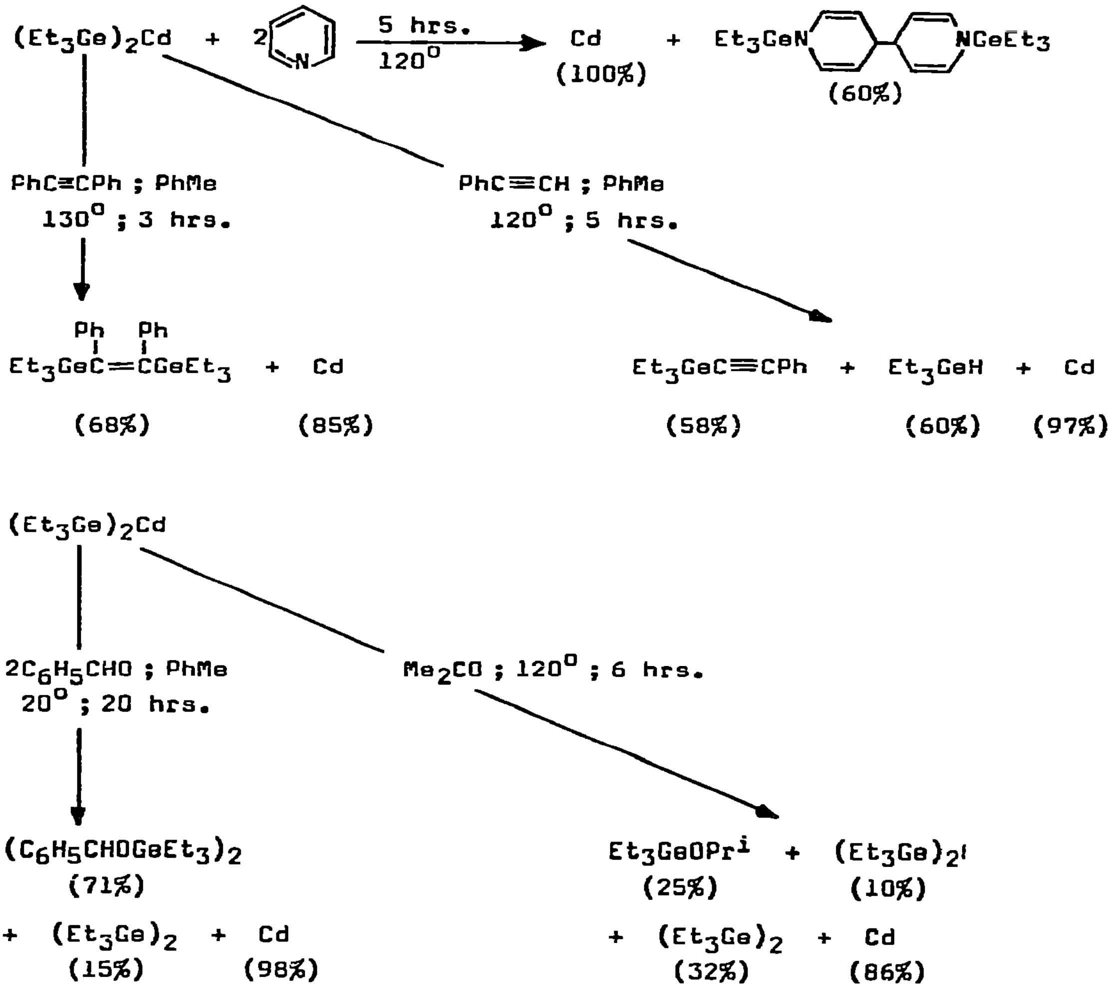


Chart 3. Some reactions of bis (triethylgermyl) cadmium.

Vyazankin et al. studied the hydrogermolysis of cadmium-carbon bonds (see AS72 ; p.231) to synthesize some germanium-cadmium bonded compounds (39) and studied their reactions. Some of their results are compiled in Chart 4.

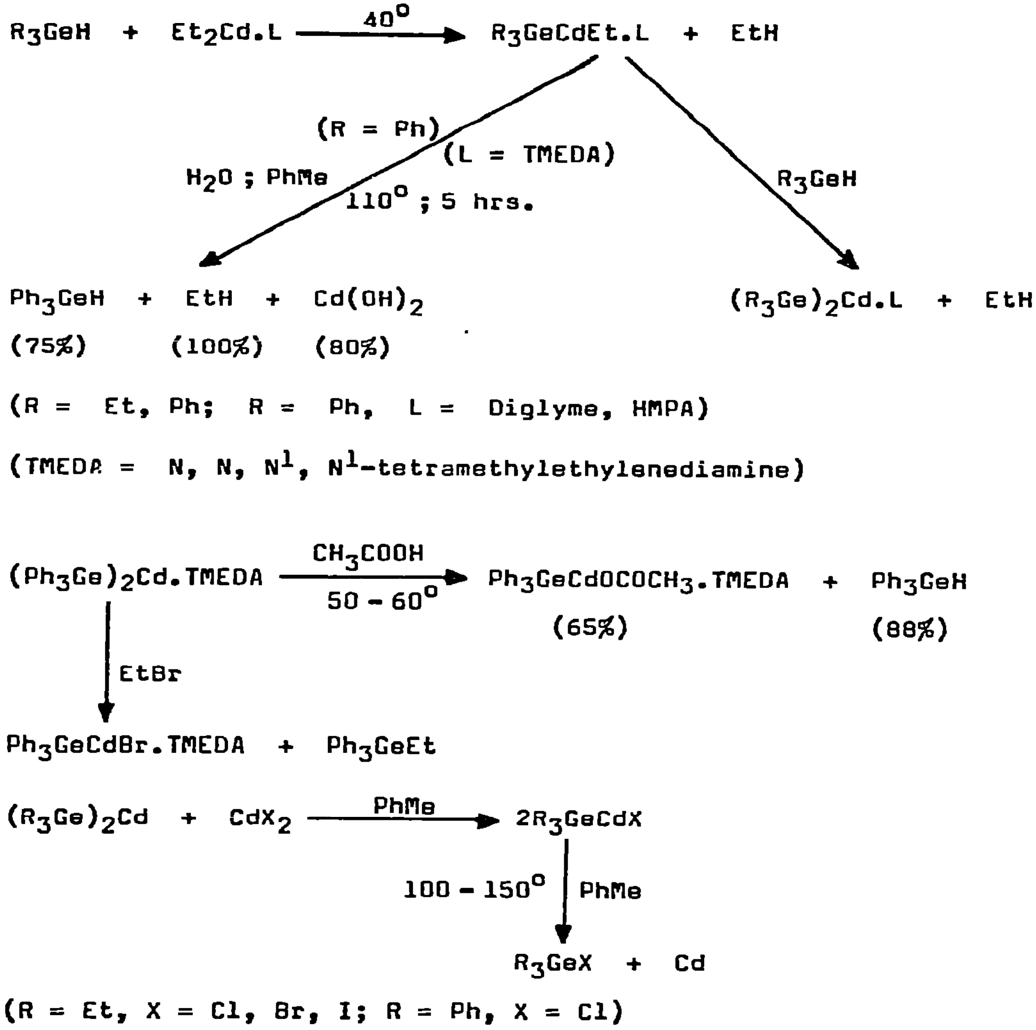
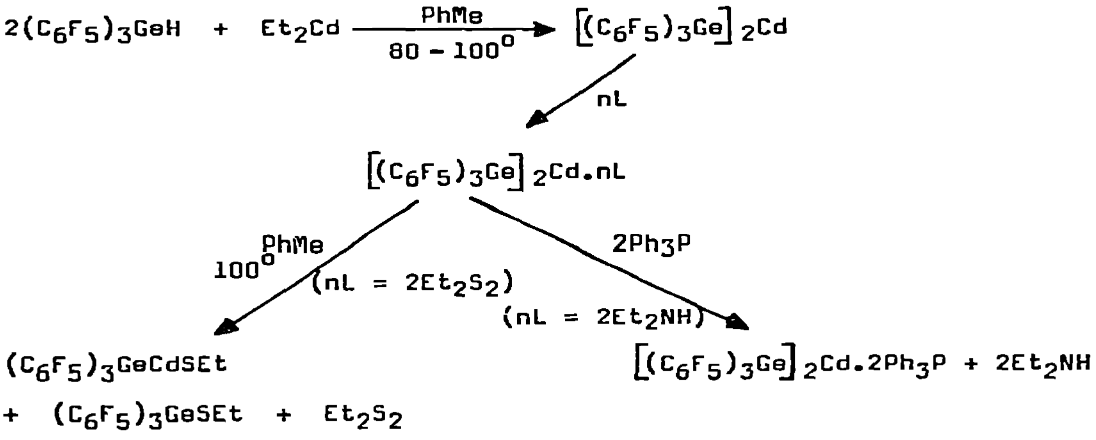


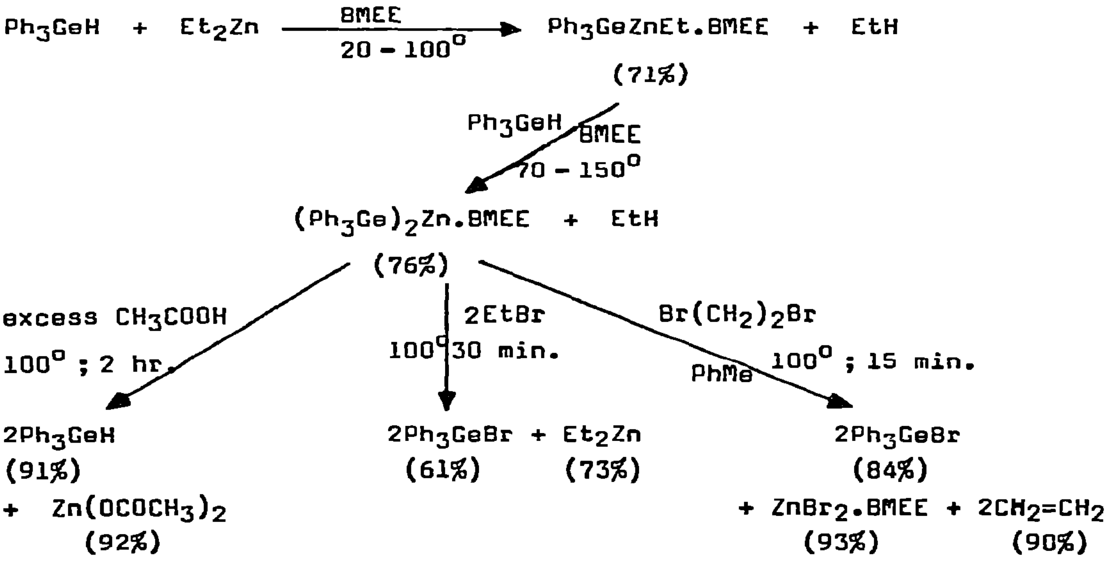
Chart 4. Synthesis and reactions of some germanium-cadmium bonded compounds.

Some complexing reactions of bis [tri (pentafluorophenyl) germyl] cadmium have been reported (29, 40):



[L = Ph_3P; $(Et_3E)_2X$ where E = Si, Ge, Sn and X = S, Se, Te; THF etc.]

The selective cleavage of the C–Zn–C grouping by triphenylgermane could be utilized to synthesize germanium-zinc bonded derivatives (41):



(BMEE = bis-2-methoxyethyl ether)

Some reactions of the alkali metal derivatives of germane have been reported (42, 43):

$$2H_3GeNa + ClCH_2CH_2Cl \longrightarrow H_3GeCH_2CH_2GeH_3 + 2NaCl$$

$$H_3GeK + ClCH_2SMe \xrightarrow{HMPT} H_3GeCH_2SMe + KCl$$

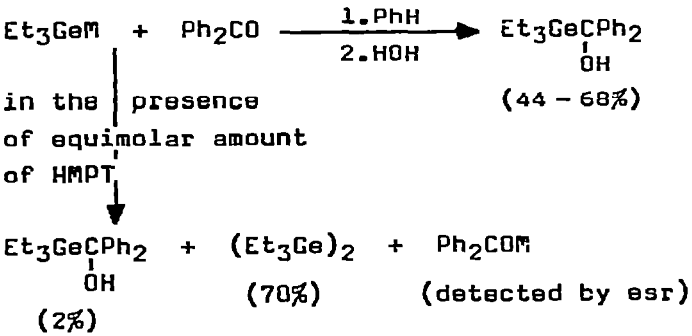
$$H_3GeK + Me_3B \xrightarrow[0^{o}]{diglyme} KGeH_3.BMe_3 \text{ (ref. 43)}$$

The preparation of solutions of trialkylgermyl-alkali metal derivatives has been accomplished (both in polar as well as nonpolar solvents) according to the reaction (44):

$$(R_3Ge)_2Hg + 2M \xrightarrow[-20^{o}\text{ ; 3 hrs.}]{PhH} 2R_3GeM + Hg$$

(R = Et, i-Pr; M = Li, Na, K)

Some reactions of these compounds are given in Chart 5.



$$Et_3GeM + Ph_2CO \xrightarrow[2.HOH]{1.PhH} Et_3Ge\underset{OH}{\underset{|}{C}}Ph_2$$

(44 – 68%)

in the presence of equimolar amount of HMPT

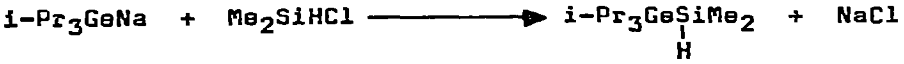
$$Et_3Ge\underset{OH}{\underset{|}{C}}Ph_2 + (Et_3Ge)_2 + Ph_2COM$$

(2%) (70%) (detected by esr)

(M = Li, K)

$$R_3GeM \xrightarrow[2.\ HOH]{1.CH_2=CH_2} R_3GeCH_2CH_3 + MOH$$

(R = Et, i-Pr; M = Li, Na, K; yield of $R_3GeC_2H_5$ decreases in going from Li to K)



$$i\text{-}Pr_3GeNa + Me_2SiHCl \longrightarrow i\text{-}Pr_3Ge\underset{H}{\underset{|}{Si}}Me_2 + NaCl$$

Chart 5. Reactions of trialkylgermyl-alkali metal derivatives.

Organometallic compounds containing metal-metal bonds (including those of germanium) have been the subject of a review (45).

Satgé and coworkers studied the thermolysis and photolysis of polygermanes and observed these reactions to provide a variety of germylgermylenes (46) which could be used for a variety of other syntheses (see Chart 6).

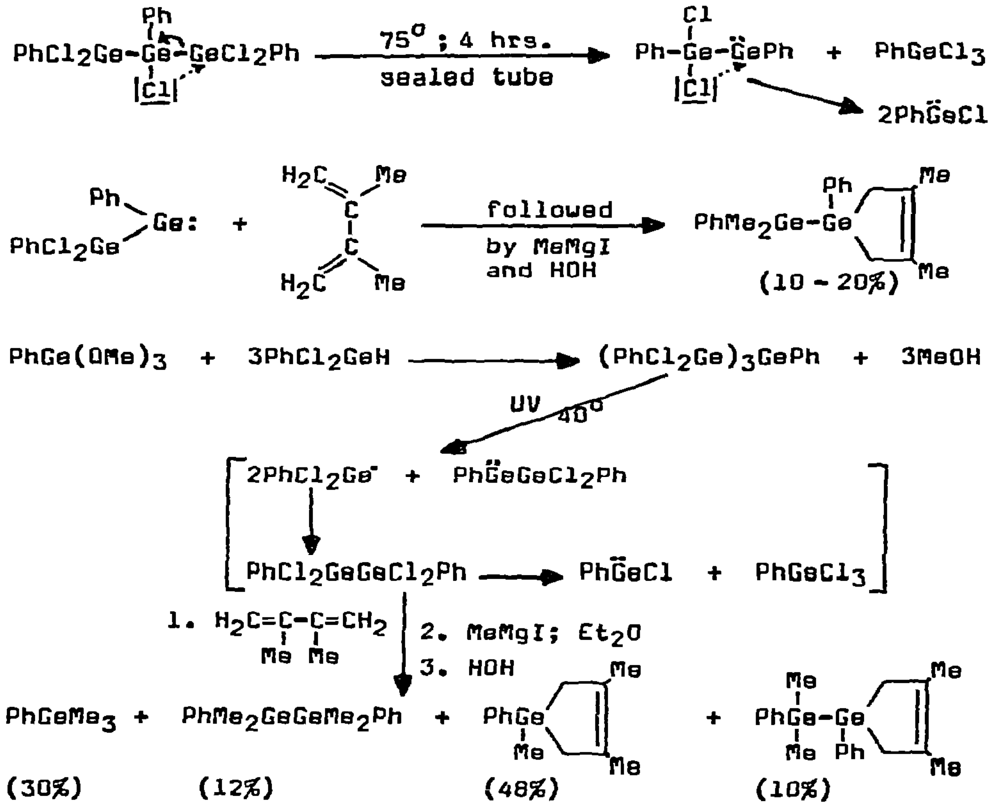


Chart 6. Reactions of polygermanes.

Some polygermanes have been synthesized according to the reaction (47):

$$C_5H_5GeH_3 + RNH_2 \text{ (or } R^1_2NH) \xrightarrow{20^\circ} \underset{(20\%)}{Ge_2H_6} + \underset{(45\%)}{Ge_3H_8} + C_5H_6$$

(R = Me, Et, CH_2Ph; R^1 = Et, n-Bu)

The normal and branched germanes of higher chain length $[Ge_nH_{2n+2}\ (n = 4, 5)]$ could be obtained by the pyrolysis of Ge_3H_8 at high temperatures ($<300°$) (48).

The results from the pyrolyses of H_3GeSiH_3 in the presence of excess (10 : 1) of $MeSiH_3$ and $MeSiD_3$ clearly demonstrate that H_3GeSiH_3 decomposed by equation [1] and possibly by equation [2] (49):

$$H_3GeSiH_3 \rightleftharpoons SiH_4 + GeH_2 \quad [1]$$

$$H_3GeSiH_3 \rightleftharpoons SiH_2 + GeH_4 \quad [2]$$

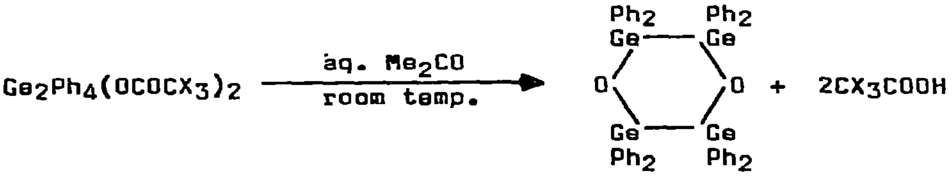
The fact that no silylene (SiH_2) insertion products were found under conditions when this diradical has been trapped suggests that step [2] is less significant.

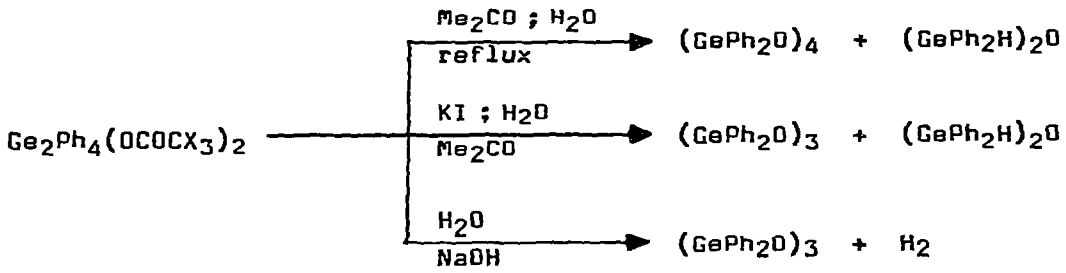
It has been shown that while hexaphenyldigermane is unreactive towards acetic acid and chloroacetic acid in boiling xylene, trichloro- and trifluoroacetic acids cleave either one or two phenyl groups according to experimental conditions (50):

$$Ph_3GeGePh_3 + X_3CCOOH \longrightarrow Ge_2Ph_5(OCOCX_3) + [GePh_2(OCOCX_3)]_2$$

$(X = F, Cl)$

The 1,2-digermanium esters are white crystalline solids unaffected by moist air over several weeks. These esters hydrolyse to cyclic oxides:





(X = F, Cl)

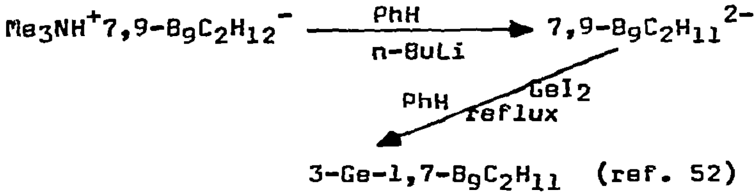
The reactions of carboranes (containing Group IV B elements) with hydrogen chloride have been shown to proceed as (51):

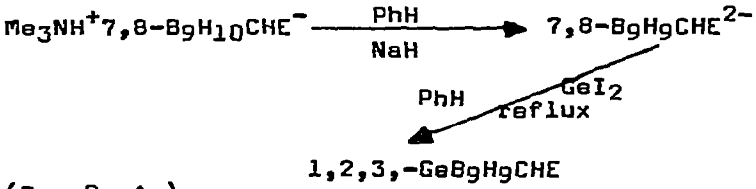
$$\mu\text{-}Me_3MC_2B_4H_7 \xrightarrow[1\ hr.]{HCl} Me_3MCl + C_2B_4H_8$$

(M = Si, Ge, Sn, Pb)

The rate of cleavage has been shown to be in the order Pb, Sn$>$Ge$>$Si. These results are viewed as a consequence of the relatively polar B-Sn and B-Pb bonds which would be expected to be highly susceptible to hydrogen chloride attack, in contrast to the less polar boron - metal bonds in silicon and germanium derivatives.

Some germacarboranes have been prepared via following reactions (52, 53):





(E = P, As)

The structures for these derivatives have been proposed on the basis of their spectral data.

The literature on the transition metal complexes containing Group IV ligands for the year 1972 has been reviewed (54).

Razuvaev et al. extended their investigations (see AS 72; p. 237) on germanium - titanium bonded derivatives and reported some of their reactions (55) (see Chart 7).

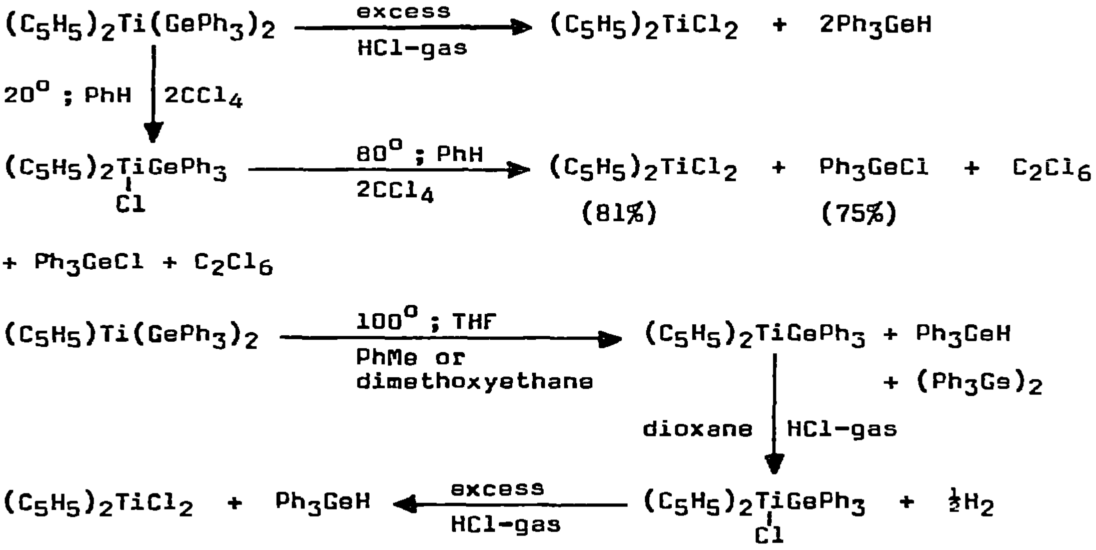


Chart 7. Reactions of germanium - titanium bonded derivatives.

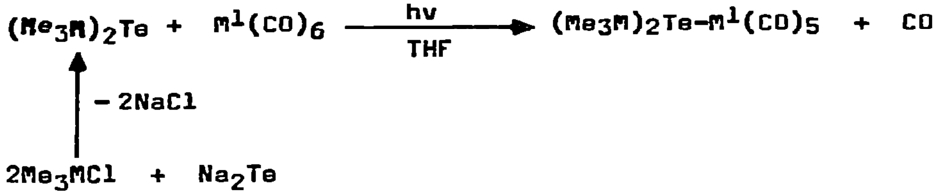
Organometal - phosphine (56), - stibine (57) and - telluride (58) substituted complexes of Cr, Mo and W have been synthesized via following routes:

$$3(Me_3M)_3P + (CH_3CN)_3M^1(CO)_3 \longrightarrow [(Me_3M)_3P]_3M^1(CO)_3 + 3CH_3CN$$

(M = Ge, Sn; M^1 = Cr, Mo; yield : 60 - 85%)

$$(Me_3M)_3Sb + M^1(CO)_6 \xrightarrow{h\nu} (Me_3M)_3Sb\text{-}M^1(CO)_5 + CO$$

(M = Ge, Sn; M^1 = Cr, Mo, W)

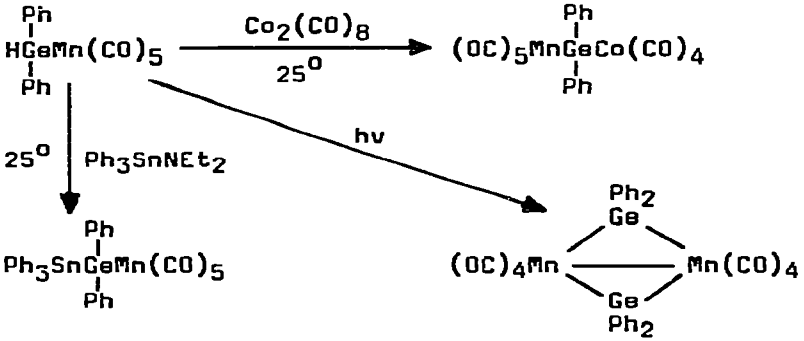


$$(Me_3M)_2Te + M^1(CO)_6 \xrightarrow[THF]{h\nu} (Me_3M)_2Te{-}M^1(CO)_5 + CO$$

$$2Me_3MCl + Na_2Te \xrightarrow{-2NaCl} (Me_3M)_2Te$$

(M = Ge, Sn, Pb; M^1 = Cr, Mo, W)

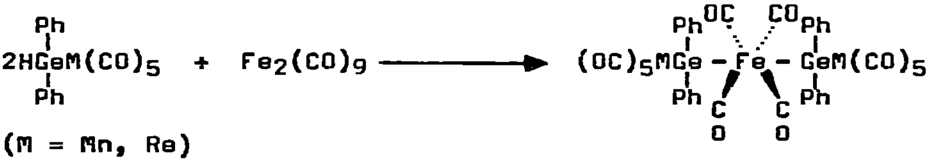
The use of some transition metal substituted germanium and tin hydrides has been made as models for metal - metal bond forming reactions toward the goal of preparing polymers with an all - metal backbone (59):



$$HGePh_2Mn(CO)_5 \xrightarrow[25^0]{Co_2(CO)_8} (OC)_5MnGePh_2Co(CO)_4$$

$$HGePh_2Mn(CO)_5 \xrightarrow[25^0]{Ph_3SnNEt_2} Ph_3SnGePh_2Mn(CO)_5$$

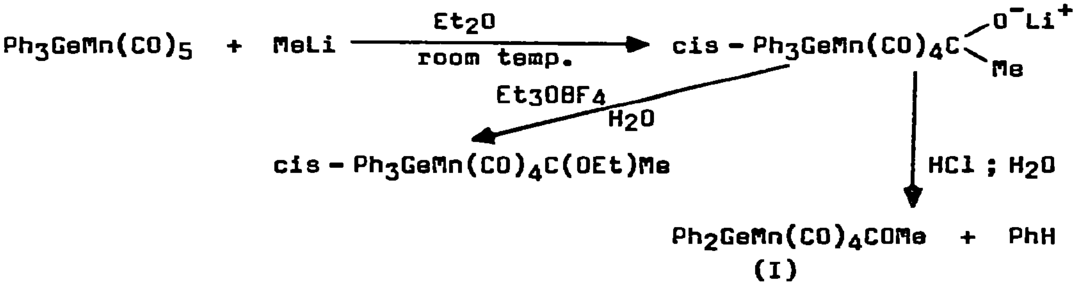
$$HGePh_2Mn(CO)_5 \xrightarrow{h\nu} [(OC)_4MnGePh_2]_2$$



$$2HGePh_2M(CO)_5 + Fe_2(CO)_9 \longrightarrow (OC)_5MGePh_2{-}Fe(CO)_4{-}GePh_2M(CO)_5$$

(M = Mn, Re)

Graham and coworkers reported the formation of carbene complexes from triphenyl- and trimethyl - germylpentacarbonylmanganese (60):

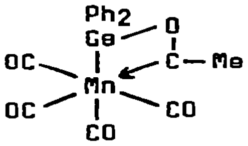


$$Ph_3GeMn(CO)_5 + MeLi \xrightarrow[\text{room temp.}]{Et_2O} cis-Ph_3GeMn(CO)_4C(O^-Li^+)Me$$

$$cis-Ph_3GeMn(CO)_4C(O^-Li^+)Me \xrightarrow[H_2O]{Et_3OBF_4} cis-Ph_3GeMn(CO)_4C(OEt)Me$$

$$cis-Ph_3GeMn(CO)_4C(O^-Li^+)Me \xrightarrow{HCl\ ;\ H_2O} Ph_2GeMn(CO)_4COMe + PhH$$

On the basis of infrared and ^{13}C - NMR spectra, (I) (which may be regarded as cyclic germoxycarbene derivative of Mn) has been assigned an alkoxide structure:

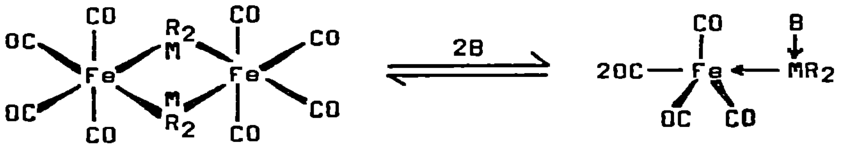


Germylpentacarbonylrhenium could be synthesized (see AS 70 ; p.213) according to the reaction (61):

$$H_3GeBr + NaRe(CO)_5 \xrightarrow{THF} H_3GeRe(CO)_5 + NaBr$$

The complex while broadly similar in properties to manganese analog, has probably a substantially stronger germanium - metal bond as reflected in the stretching force - constant, the increased thermal and chemical stability and the changes in the fragmentation pattern.

Using infrared spectroscopy, it has been shown that molecules of the general formula $[R_2MFe(CO)_4]_2$ (M = Ge, Sn, Pb) readily and reversibly undergo homolytic cleavage by relatively weak Lewis bases to produce tetracarbonyliron complexes (62):



(R = Me, n-Bu, t-Bu, Ph; M = Ge, Sn, Pb; B = tetrahydrofuran, acetone, diethyl ether, dimethylformamide, pyridine, acetonitrile)

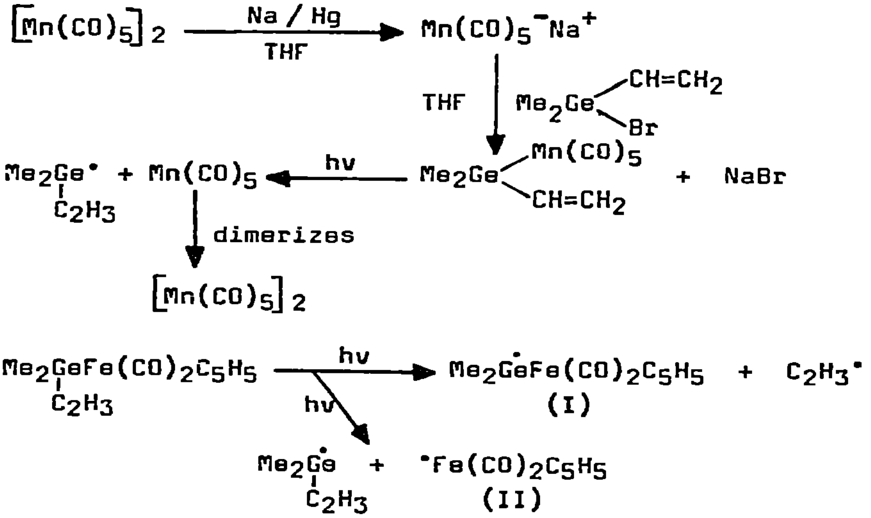
The relative cleavage propensity for metals is Ge>Sn≥Pb and for the bases is pyridine>acetone>tetrahydrofuran>diethyl ether.

The preparation of some heterotrimetallic derivatives has been accomplished via the reaction (63):

$$\begin{tikzcd} C_5H_5Fe(CO)_2MX_3 + [C_5H_5Ni(CO)]_2 \arrow[d, "\text{reflux}"', "\text{PhH}"] \\ C_5H_5Fe(CO)_2MX_2Ni(CO)(C_5H_5) + C_5H_5Ni(CO)X \end{tikzcd}$$

(M = Ge, Sn; X = Cl, Br)

Job and Curtis studied the photolysis of vinyl-substituted germanium derivatives of transition metal carbonyls (64, 65). These complexes [$Me_2Ge(C_2H_3)M$; where M = $Mn(CO)_5$, $Mo(CO)_3(\pi-C_5H_5)$, $Co(CO)_4$, $Fe(CO)_3NO$, $Co(CO)_2(NO)(CN)$, $Fe(CO)_2(\pi-C_5H_5)$; $Mn(CO)_4PPh_3$ and $Co(CO)_3PPh_3$] show no tendency to rearrange to π-allyl complexes, instead transition metal carbonyl dimers, formed by scission of the germanium-metal bond are the most common products formed when these complexes are subjected to photolysis or pyrolysis. Some of their results are summarized in Chart 8.



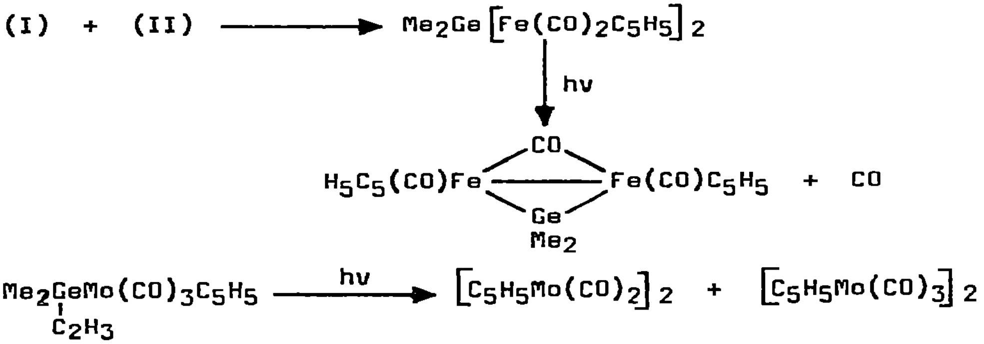


Chart 8. Photochemistry of vinyl-substituted germanium derivatives of transition metal carbonyls.

Some germanium-nickel complexes have been synthesized and their reactions studied (66):

$$\begin{tikzcd} \pi\text{-}C_5H_5(X)(L)Ni + HGeX_3 \text{ (or } CsGeX_3 \text{ or } Ph_3GeLi) \arrow[d] \\ \pi\text{-}C_5H_5(R_3Ge)(L)Ni \end{tikzcd}$$

($R_3Ge = X_3Ge$, Ph_3Ge; X = halide; L = $R^1{}_3P$ or $R^1{}_3As$; R^1 = Et, Ph)

$$\begin{tikzcd} \pi\text{-}C_5H_5(Cl_3Ge)(Ph_3P)Ni \arrow[d, "\substack{Ph_2Hg \\ PhH}"', "\substack{reflux \\ 12\ hrs.}"] \arrow[dr, "\substack{PhH \\ reflux\ 2\ hrs.}", "Et_4Pb"'] & \\ \pi\text{-}C_5H_5(PhCl_2Ge)(Ph_3P)Ni + PhHgCl & \pi\text{-}C_5H_5(EtCl_2Ge)(Ph_3P)Ni + Et_3PbCl \end{tikzcd}$$

The reduction of $Os_3(CO)_{12}$ by sodium in liquid ammonia gave a cream solid which reacted with halides to give good yields of $Os(CO)_4X_2$ (X = Me, H_3Ge, Ph_3Sn, Me_3Pb etc.) and lower yields of $Os(CO)_4XH$ (X = Me, H_3Ge, Me_3Sn) (67).

Ebsworth and Leitch observed that trans-$Ir(CO)Cl(PPh_3)_2$ reacted with SiH_3X (X = H, Cl, Br, I) and GeH_4 in benzene at room temperature to give insoluble 1 : 1 adducts. With GeH_3Y (Y = Cl, Br, I) and Ge_2H_6 initial reaction gave soluble 1 : 1 adducts, the stereochemistry of which was determined by NMR spectroscopy, insoluble adducts precipitated after 30 - 60 min. (68).

Germanium - nitrogen compounds

The preparation and reactions of a variety of germylhydrazines and germyldiazenes have been reported (69). These are listed in Chart 9.

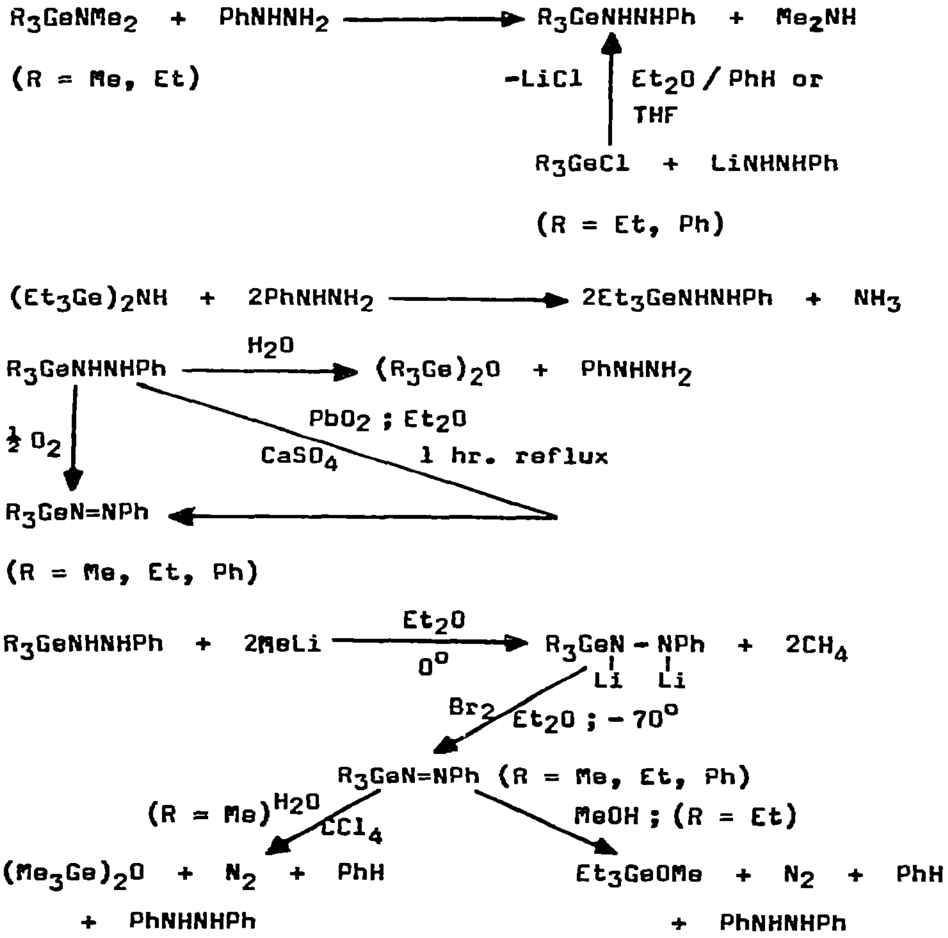
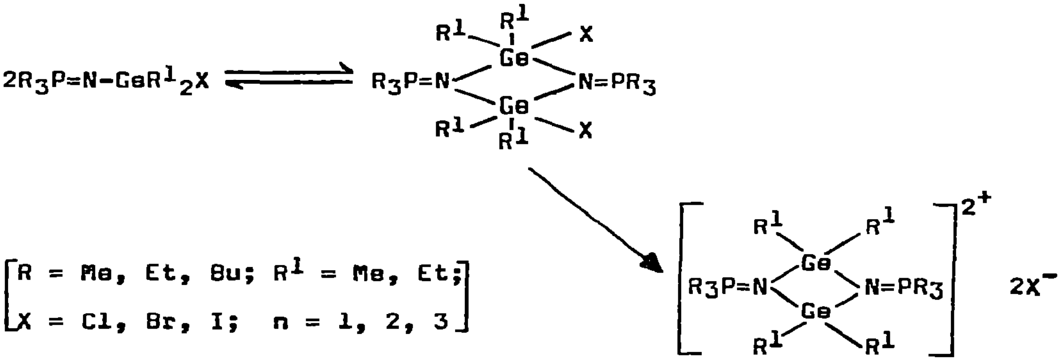


Chart 9. Synthesis and reactions of germylhydrazines and germyldiazenes.

The phosphinimine derivatives of germanium could be synthesized according to the exchange reaction (70):

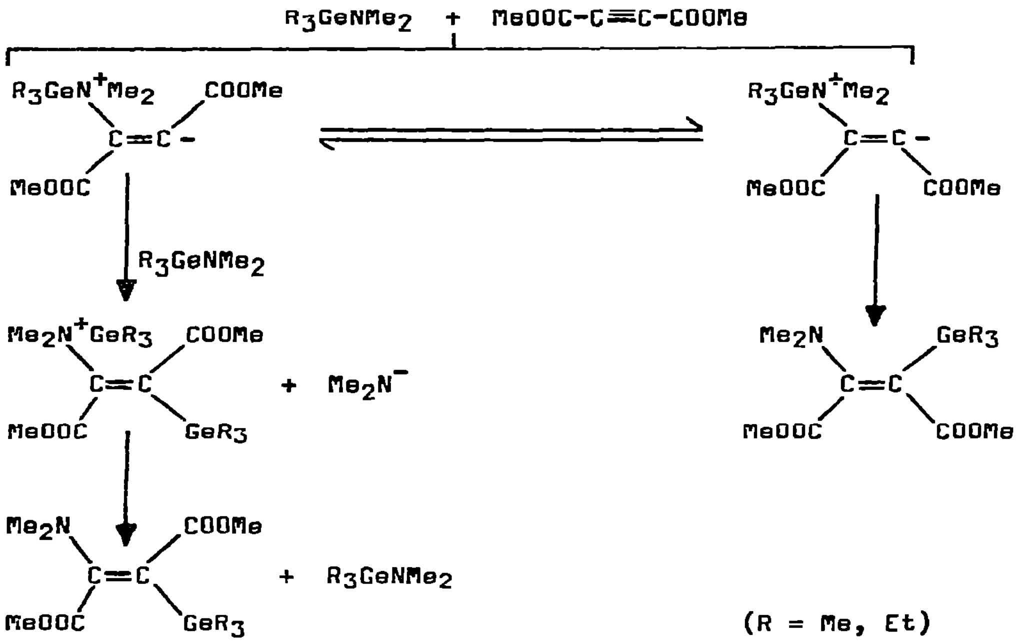
$$R^1_{3-n}GeX_{n+1} + R_3P{=}NSiMe_3 \xrightarrow{CH_2Cl_2} R_3P{=}N{-}GeR^1_{3-n}X_n + Me_3SiX$$

These rearrange as:



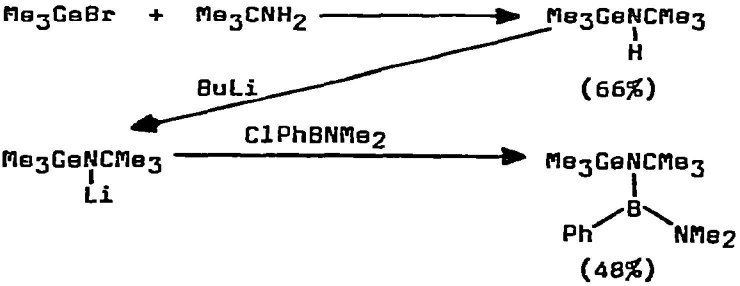
$\left[\begin{array}{l} R = Me,\ Et,\ Bu;\ R^1 = Me,\ Et; \\ X = Cl,\ Br,\ I;\ \ n = 1,\ 2,\ 3 \end{array}\right]$

It has been shown that dimethyl (triorganogermyl) amines add to the triple bond of acetylenedicarboxylic esters, leading to the two isomers. The mechanism, of an ionic nature, involves an initial nucleophilic attack of the nitrogen atom onto acetylenic carbon and formation of a bipole in equilibrium under two forms by an allenic intermediate form (71).



(R = Me, Et)

The preparation of some N - trimethyl - Group IV substituted aminoboranes (72) and 1,1 - bis (trifluoromethyl) methyleneamido complexes containing Group IV B elements (73) has been accomplished via following reactions:

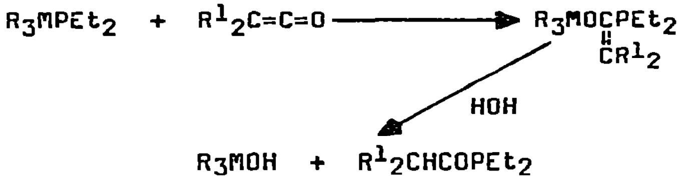


$$Me_{4-n}MCl_n + nLiN{=}C(CF_3)_2 \longrightarrow Me_{4-n}M\left[N{=}C(CF_3)_2\right]_n + nLiCl$$

(M = Si, Ge, Sn ; n = 1 - 4)

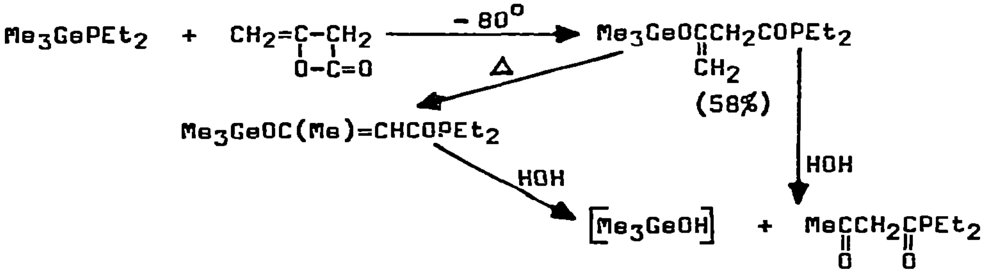
Germanium – phosphorus, –arsenic and –antimony compounds

Satgé and coworkers (107) extended their investigations on the addition reactions of organogermylphosphines (see AS 72 ; p.246) and observed the addition of ketenes to germyl – and silylphosphines with opening of the carbonyl group and formation of phosphorylated alkenoxygermanes or –silanes (74):



(R = Me, Et ; R^1 = H, Ph ; M = Si, Ge)

Diketene also reacts with germyl – and silylphosphines with acyl – oxygen bond cleavage and formation of metallated and phosphorylated ketoenolates which isomerize either partially (M = Si) or completely (M = Ge):



It is interesting to note that germylamines gave C – derivatives in their reactions with ketene and a mixture of O – and C – derivatives with diphenylketene whereas germylphosphines (as shown above) give exclusively the O – derivatives.

Some organo – Group IV phosphines have been synthesized according to the reaction scheme (75):

$$Me_3MCl + (Me_3C)_2PCl + Mg \xrightarrow{HMPTA} Me_3MP(CMe_3)_2 + MgCl_2$$

$$\begin{bmatrix} M = Si,\ Ge,\ Sn\ ;\ yield:\ 36-95\% \\ HMPTA = \text{hexamethylphosphoric triamide} \end{bmatrix}$$

The reactions of some Group IV B element-phosphorus bonded derivatives have been utilised to synthesize trifluoromethyl-phosphines and -arsines of these elements (76-78). Some of their results are summarized in Chart 10.

$$\begin{tikzcd}
Me_3MPH_2 \arrow[r, "HQ(CF_3)_2"] \arrow[d, "H_2QCF_3"] \arrow[dr, "(CF_3)_2QX"] & Me_3MQ(CF_3)_2 \\
Me_3MQHCF_3 & (CF_3)_2QPH_2
\end{tikzcd}$$

$$(Me_3M)_3P + H_2QCF_3 \longrightarrow (Me_3M)_2QCF_3$$

$$Me_3MP(CF_3)_2 + H_2AsCF_3 \longrightarrow Me_3MAsHCF_3$$

$(M = Si, Ge, Sn;\ Q = P, As;\ X = Cl, Br, I)$

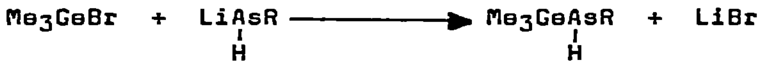
The reaction rate depends on M $(Si < Ge < Sn)$ and Q $(P < As)$.

Chart 10. Synthesis of some trifluoromethyl- phosphine and -arsine derivatives of Group IV B elements.

Drake and Anderson accomplished the synthesis of some new secondary germanium arsines and mixed germanium-tin arsines according to following reactions (79):

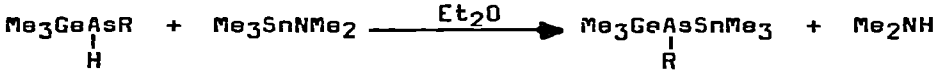
$$\begin{tikzcd}
(Me_3Ge)_2AsR + MeLi \arrow[r, "Et_2O\ ;\ 5\ hrs."', "room\ temp."'] & Me_3Ge\underset{\mid\atop Li}{As}R + Me_4Ge \arrow[d, "MeSH"', "room\ temp."] \\
 & Me_3Ge\underset{\mid\atop H}{As}R + MeSLi
\end{tikzcd}$$

$(R = Me, Ph)$



$$\mathrm{Me_3GeBr} + \mathrm{Li\underset{H}{As}R} \longrightarrow \mathrm{Me_3Ge\underset{H}{As}R} + \mathrm{LiBr}$$

(R = Me, Ph)



$$\mathrm{Me_3Ge\underset{H}{As}R} + \mathrm{Me_3SnNMe_2} \xrightarrow{\mathrm{Et_2O}} \mathrm{Me_3Ge\underset{R}{As}SnMe_3} + \mathrm{Me_2NH}$$

(R = Me, Ph, Me$_3$Ge)

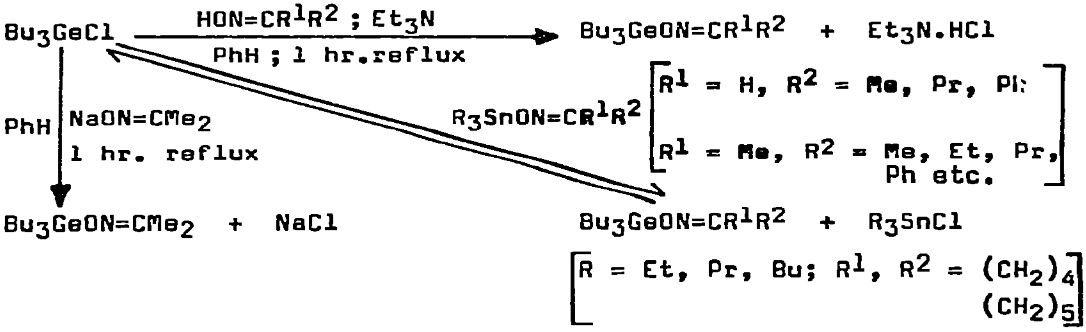
$$\mathrm{Me_2M(NMe_2)_2} + 2\mathrm{(Me_3Ge)_2AsH} \longrightarrow \mathrm{[(Me_3Ge)_2As]_2MMe_2} + 2\mathrm{Me_2NH}$$

(M = Ge, Sn)

The reactions of tris(trimethylgermyl)phosphine (56) and -stibine (57) with some transition metal carbonyls have been reported (see p.19).

Germanium - oxygen compounds

Mehrotra et al. reported various preparative routes to tributylgermanium oximates and studied some of their reactions (80). These are compiled in Chart 11.



$$\mathrm{Bu_3GeCl} \xrightarrow[\mathrm{PhH\ ;\ 1\ hr.reflux}]{\mathrm{HON{=}CR^1R^2\ ;\ Et_3N}} \mathrm{Bu_3GeON{=}CR^1R^2} + \mathrm{Et_3N.HCl}$$

$\left[\mathrm{R^1 = H,\ R^2 = Me,\ Pr,\ Ph}\quad \mathrm{R^1 = Me,\ R^2 = Me,\ Et,\ Pr,\ Ph\ etc.}\right]$

$$\mathrm{Bu_3GeCl} \xrightarrow[\mathrm{1\ hr.\ reflux}]{\mathrm{PhH}\ \mathrm{NaON{=}CMe_2}} \mathrm{Bu_3GeON{=}CMe_2} + \mathrm{NaCl}$$

$$\mathrm{Bu_3GeCl} \overset{\mathrm{R_3SnON{=}CR^1R^2}}{\rightleftharpoons} \mathrm{Bu_3GeON{=}CR^1R^2} + \mathrm{R_3SnCl}$$

$\left[\mathrm{R = Et,\ Pr,\ Bu;\ R^1,\ R^2 = (CH_2)_4,\ (CH_2)_5}\right]$

$$\mathrm{Bu_3GeOEt} + \mathrm{HON{=}CR^1R^2} \xrightarrow[\mathrm{PhH\ ;\ 4\ hrs.\ reflux}]{p\text{-toluenesulphonic acid}} \mathrm{Bu_3GeON{=}CR^1R^2} + \mathrm{EtOH}$$

[R^1, R^2 = Me, Me; Me, Et; (CH$_2$)$_4$; (CH$_2$)$_5$]

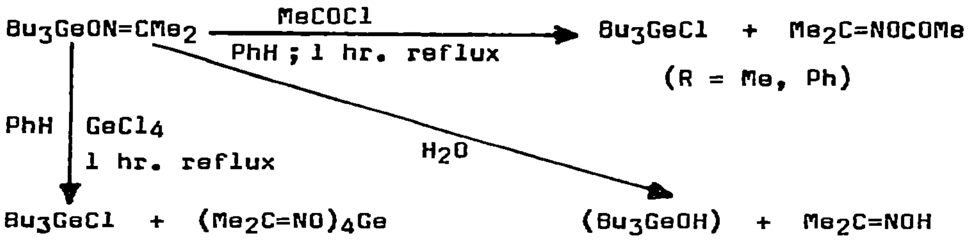
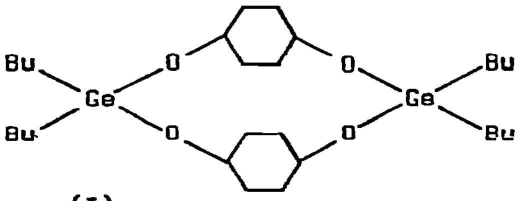
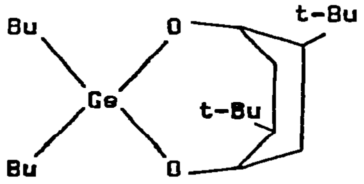


Chart 11. Preparation and reactions of tributylgermanium oximates.

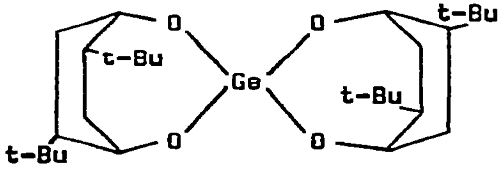
Cyclic organogermanium compounds of the type $[GeBu_2-O-(c-C_6H_{10})-O]_n$ have been prepared by reaction in mole ratio 1 : 1 of dibutyl-germanium dichloride with cis-1, 4-cyclohexanediol in benzene in the presence of a hydrogen halide acceptor (81). The ring size has been found to vary with concentration of the reaction solution and the temperature. The dimer (I) has been isolated in extremely dilute solution. In contrast, the reactions of dibutylgermanium dichloride and germanium tetrachloride with cis, cis, cis-2, 5-di-tert.butyl-1, 4-cyclohexanediol in mole ratios 1 : 1 and 1 : 2 respectively, gave only monomeric products [(II) and (III) respectively]. The difference may be associated with the boat conformation of the diol favoured in this case. The structures have been proposed on the basis of spectral data.



(I)



(II)

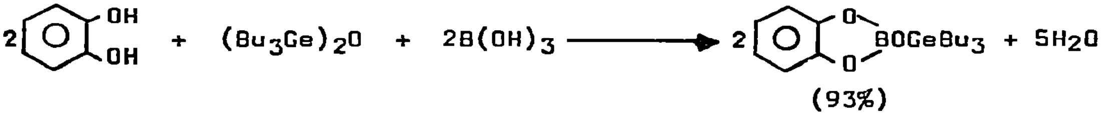


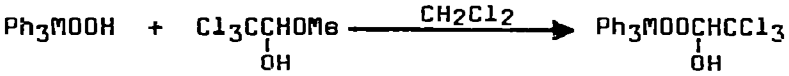
(III)

Pentafluoroorthotellurates (82) of silicon and germanium, germoboroxanes (83) and α-hydroxyperoxides containing silicon and germanium (84) have been prepared via following reactions:

$$Me_3GeCl + AgOTeF_5 \xrightarrow{\text{acetonitrile}} Me_3GeOTeF_5 + AgCl$$

$$3(Bu_3Ge)_2O + 2B(OH)_3 \xrightarrow[\text{reflux}]{\text{PhH ; 12 hrs.}} \underset{(97\%)}{2(Bu_3GeO)_3B} + 3H_2O$$



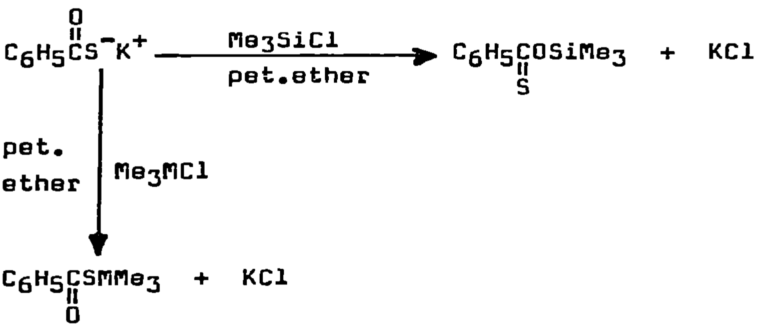


$$Ph_3MOOH + Cl_3C\underset{OH}{\underset{|}{C}}HOMe \xrightarrow{CH_2Cl_2} Ph_3MOO\underset{OH}{\underset{|}{C}}HCCl_3$$

[M = Ge (85%); M = Si (30%)]

Germanium-sulfur, -selenium and -tellurium compounds

Ishii and coworkers found that the reactions of potassium salts of aromatic thio acid with chlorotrimethylsilane gave the corresponding thionoacyloxysilanes whereas analogous reactions with chloromethylgermane or -stannane gave the corresponding thiol esters containing the sulfur-metal linkage in almost quantitative yields (85):



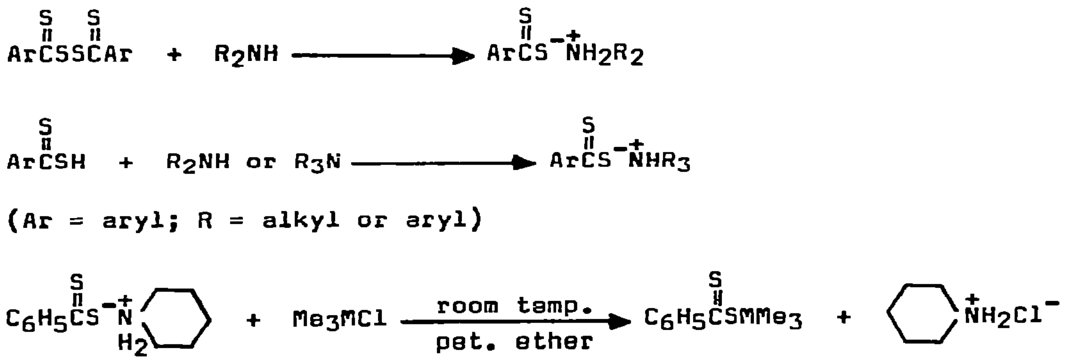
$$C_6H_5\overset{O}{\overset{\|}{C}}S^-K^+ \xrightarrow[\text{pet.ether}]{Me_3SiCl} C_6H_5\underset{S}{\underset{\|}{C}}OSiMe_3 + KCl$$

$$C_6H_5\overset{O}{\overset{\|}{C}}S^-K^+ \xrightarrow[\text{pet. ether}]{Me_3MCl} C_6H_5\underset{O}{\underset{\|}{C}}SMMe_3 + KCl$$

(M = Ge, Sn)

The method has been used to synthesize a variety of substituted (benzoylthio) trimethylgermanes, $XC_6H_4\underset{\underset{O}{\|}}{C}SGeMe_3$ (where X = $p-NO_2$, $m-Cl$, $p-Me$, $m-Me$ etc.).

The authors have also synthesized some trimethylmetal (IV B) esters of dithio acids according to the reaction scheme (86):



$$Ar\overset{\overset{S}{\|}}{C}S\overset{\overset{S}{\|}}{C}Ar + R_2NH \longrightarrow Ar\overset{\overset{S}{\|}}{C}S^{-}\overset{+}{N}H_2R_2$$

$$Ar\overset{\overset{S}{\|}}{C}SH + R_2NH \text{ or } R_3N \longrightarrow Ar\overset{\overset{S}{\|}}{C}S^{-}\overset{+}{N}HR_3$$

(Ar = aryl; R = alkyl or aryl)

The preparation of a number of methylseleno derivatives of Group IV B elements has been accomplished via following routes (87):

$$Me_3MNMe_2 + MeSeH \xrightarrow[\text{or PhH}]{\text{PhMe}} Me_3MSeMe + Me_2NH$$

(M = Si, Ge, Sn)

$$nMe_3SiSeMe + Me_{4-n}MX_n \longrightarrow Me_{4-n}M(SeMe)_n + nMe_3SiX$$

(M=Ge, Sn; n = 1 - 4; X = F, Cl, Br)

$$\begin{tikzcd} 4MeSeH + LiAlH_4 \arrow[r, "Et_2O"] & LiAl(SeMe)_4 + 4H_2 \arrow[dl, "4Me_3MX"] \\ 4Me_3MSeMe + LiX + AlX_3 & \end{tikzcd}$$

(M = Si, Ge, Sn; X = Cl, Br)

Some reactions of organometallic chalcogenides with ethyllithium have been shown to proceed exothermally (88):

$$\begin{tikzcd}
\mathrm{Et_3MXH} + \mathrm{EtLi} \arrow[r, "\text{hexane}"] & \underset{(\mathrm{I})}{\mathrm{Et_3MXLi}} + \mathrm{EtH} \arrow[dl, "n-\mathrm{BuCl}"] \\
\mathrm{Et_3MXBu^n} + \mathrm{LiCl} &
\end{tikzcd}$$

(M = Si, Ge; X = S, Se, Te)

$$(\mathrm{Et_3M})_2\mathrm{Se} + \mathrm{EtLi} \longrightarrow \underset{(\mathrm{I})}{\mathrm{Et_3MSeLi}} + \mathrm{Et_4M}$$

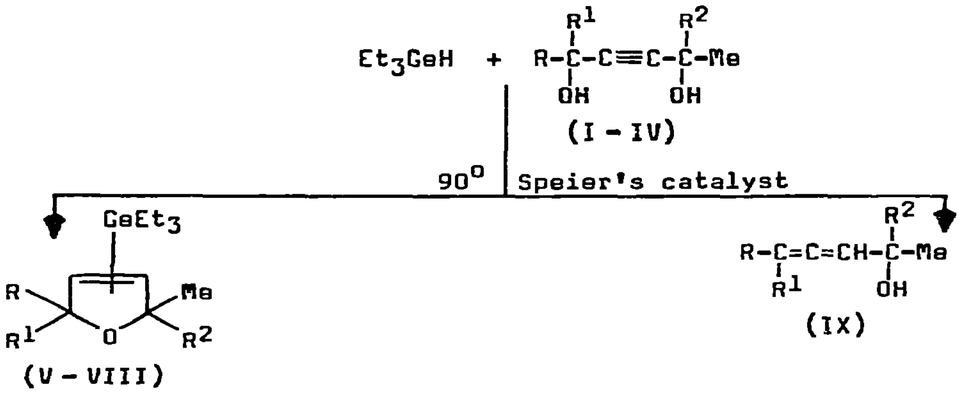
(M = Si, Ge)

The compounds (I) are associated which probably results from the occurrence of donor - acceptor interaction between the chalcogen atoms and lithium.

Schumann et al. synthesized some pentacarbonyl (organometallic telluride) - Cr, Mo and W complexes (58) (see p. 19).

Alkenyl - and alkynyl - germanium compounds

Hydrogermylation of some naphthyl - containing di - tertiary acetylenic γ- glycols has been shown to involve complete dehydration of the expected adduct with formation of the dihydrofurans (89).
In the case of the symmetrical glycol (IV), the product (IX) formed as a result of the β-breakdown of the addition product has also been isolated.



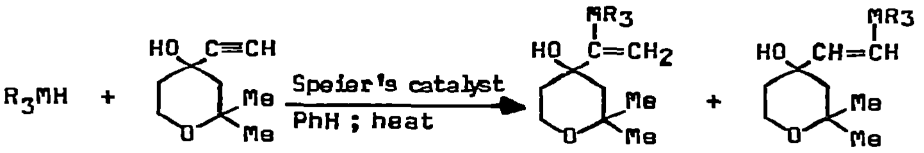
$R = R^1 = Me$; $R^2 = 1-C_{10}H_7$ (V)
$R = R^1 = Me$; $R^2 = 2-C_{10}H_7$ (VI)
$R = Me$; $R^1 = Pr$; $R^2 = 2-C_{10}H_7$ (VII)
$R = Me$; $R^1 = R^2 = 2-C_{10}H_7$ (VIII)
$R = Me$; R^1, $R^2 = 2-C_{10}H_7$ (IX)

The use has been made of PMR spectra to establish the orientation in the addition of triethylgermane at the triple bond and to determine the ratio of the isomers.

The addition reactions of organohydrogermanes to alkynyl compounds could be used as convenient synthetic routes to alkenyl-germanium derivatives (90-92):

$$R_3GeH + BuOC\equiv CH \longrightarrow R_3GeCH{=}CHOBu$$

(R = alkyl group)



($R_3 = Et_3, EtBu_2$; M = Si, Ge)

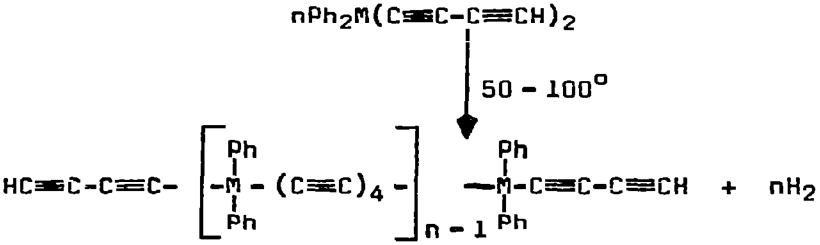
Eisch and Gupta observed that lithiation of vinylic Group IV B organometalloidal compounds gives anion-radicals which, if quenched quickly, give synthetically useful bimolecular coupling (93):

$$Ph_3GeCH{=}CH_2 \xrightarrow[t\text{-}BuOH/THF]{-75^{\circ}\,;\,Li} \underset{(60\%)}{Ph_3GeCH_2Me} + \underset{\text{(small amount)}}{Ph_3GeH} + \underset{(35\%)}{\begin{array}{c} Ph_3GeCH_2CH_2 \\ | \\ Ph_3GeCH_2CH_2 \end{array}}$$

The radical-anions, $Ph_3M\ddot{C}H\text{-}\dot{C}H_2$ (detected by esr) seem to decrease in stability as M= Si, Ge or Sn, successively.

The thermal dehydropolycondensation of diethynyl derivatives of silicon and germanium has been shown to give polymers containing four acetylenic groupings between the heteroatoms (94):

$$HC{\equiv}C\text{-}C{\equiv}CH \;+\; EtMgBr \;+\; Ph_2MCl_2 \xrightarrow[THF]{0-5^{\circ}} Ph_2M(C{\equiv}C\text{-}C{\equiv}CH)_2$$



$$nPh_2M(C{\equiv}C\text{-}C{\equiv}CH)_2 \xrightarrow{50-100^{\circ}} HC{\equiv}C\text{-}C{\equiv}C\text{-}\left[\text{-}\underset{Ph}{\overset{Ph}{M}}\text{-}(C{\equiv}C)_4\text{-}\right]_{n-1}\text{-}\underset{Ph}{\overset{Ph}{M}}\text{-}C{\equiv}C\text{-}C{\equiv}CH \;+\; nH_2$$

(M = Si, Ge)

Oxidative coupling reactions of some Group IV B acetylenes have been reported (95):

$$Me_3MC{\equiv}CH \xrightarrow[TMEDA\,;\,Me_2CO]{CuCl\,;\,O_2} Me_3MC{\equiv}C\text{-}C{\equiv}CMMe_3$$

(M = C, Si, Ge)
(TMEDA = N, N, N^1, N^1 - tetramethylethylenediamine)

Germacyclanes

A variety of new diorganogermanium intermediates have been characterized and their condensation reactions with 2, 3 - dimethyl - butadiene (DMB) used in the synthesis of cyclic germanium compounds

(46, 96) (see also p. 16). Some of these reactions are given in Chart 12.

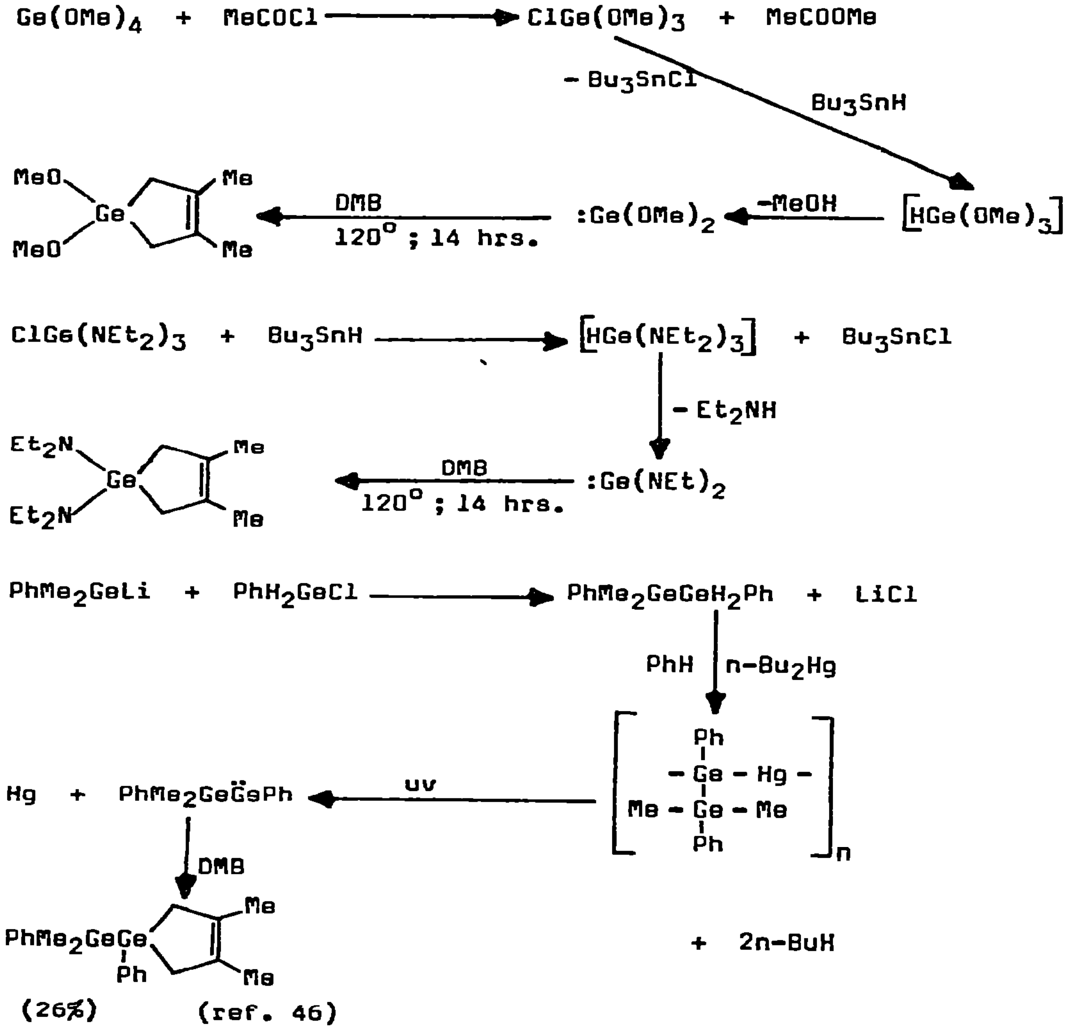
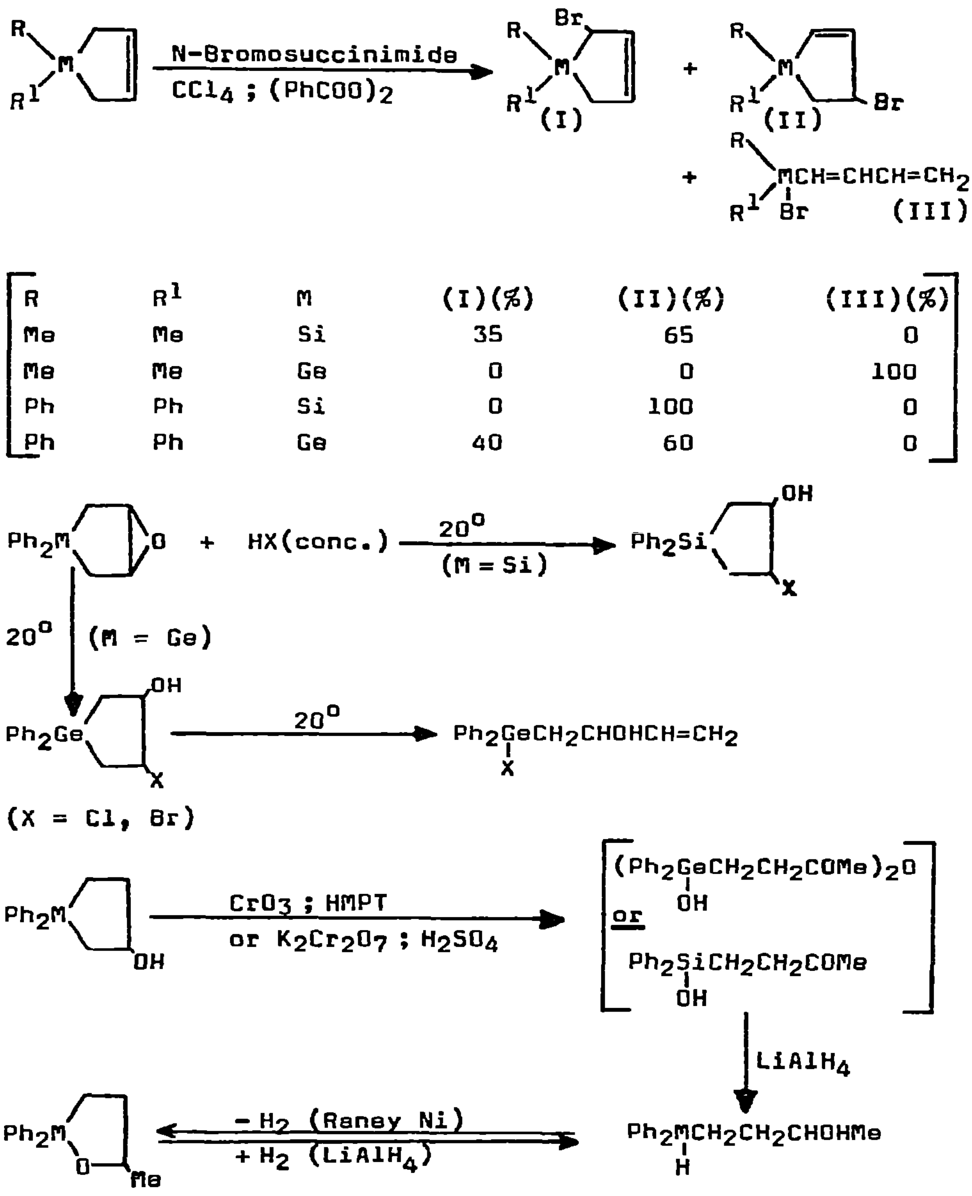


Chart 12. Synthesis of some germacyclanes.

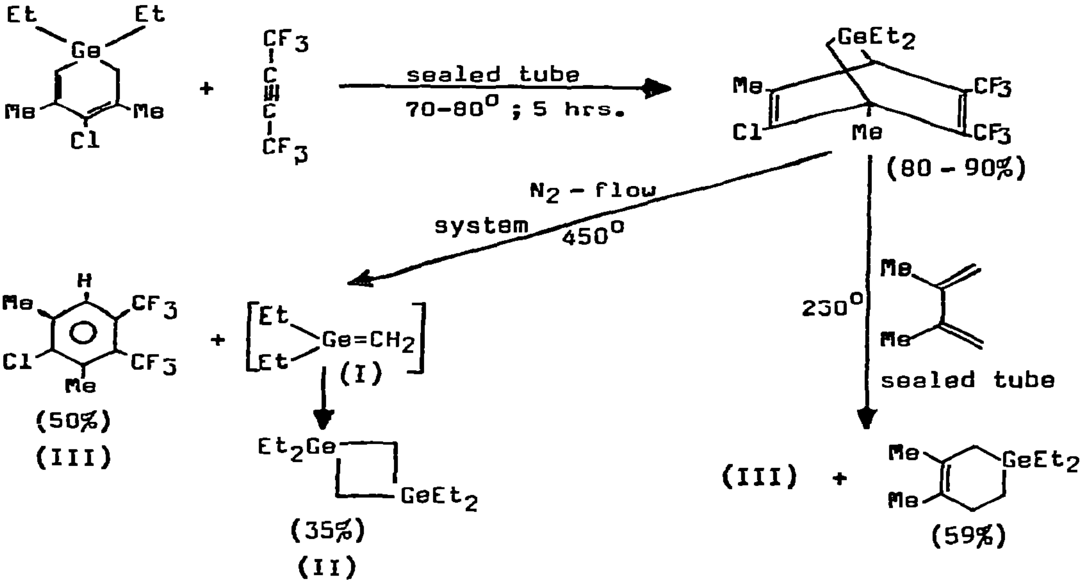
Mazerolles et al. reported that the synthesis and chemical reactivity of 1-sila- and 1-germa-3-cyclopentenes (97, 98), 6-oxa-3-sila and -3-germabicyclo [3.1.0] hexanes (98) and 1-sila- and 1-germa-3-cyclopentanols (98) are closely dependent upon the heteroatom and its substituents. The authors have made an extensive use of NMR spectroscopy to characterize and evaluate the relative amounts of various products formed in the reactions of these compounds. Various reactions are listed in Chart 13.



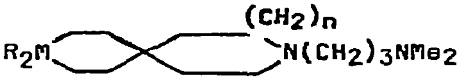
R	R^1	M	(I)(%)	(II)(%)	(III)(%)
Me	Me	Si	35	65	0
Me	Me	Ge	0	0	100
Ph	Ph	Si	0	100	0
Ph	Ph	Ge	40	60	0

Chart 13. Some reactions of germacyclanes.

The reactions of substituted germacyclohexadiene with a two fold excess of perfluoro – 2 – butyne followed by thermolysis of the product has been shown to give the digermacyclobutane derivative (II). The formation of (II) has been argued for the intermediacy of (I) and thus providing an evidence for a germanium – carbon (p – p double bond (99).



The preparation of some silicon and germanium containing metal azaspiro [4, 5] – decanes of the type:

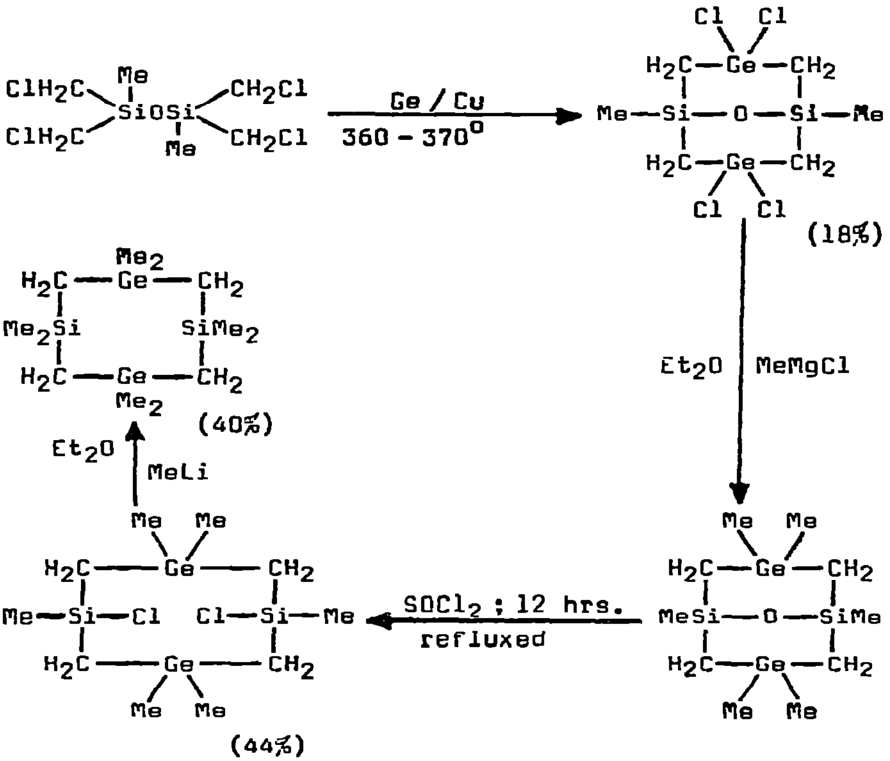


$R_2M(CH_2)_4C(CH_2)_n(CH_2)_2N(CH_2)_3NMe_2$

(R = Me; M = Si; n = 0, 1 and R = Et; M = Ge; n = 0)

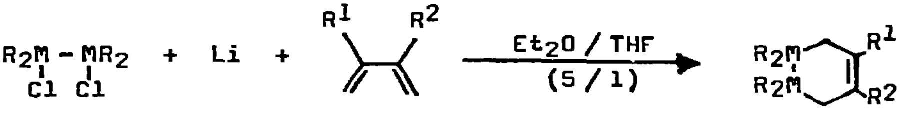
has been patented (100).

Mironov et al. continued their studies on 'direct synthesis' reactions (see AS 72; p.260) for synthesizing heterocyclic compounds containing silicon and germanium and reported the following reactions (101):

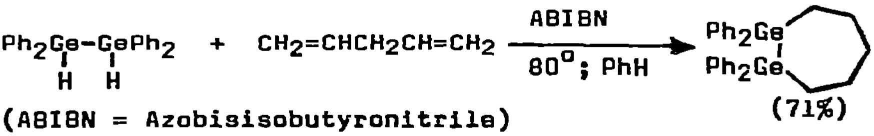


The preparation and reactions of some 1, 4 - digermacyclohexadienes have been the subject of a Ph.D. thesis (19) (see also AS 72; p.262).

Some reactions of organodigermanes (102) and cycloaddition of organodihydrodigermanes to 1, 4 - pentadiene (103) have been shown to provide convenient routes to 1, 2 - digermacyclanes.



[R = Me, Et; R^1 = R^2 = H, Me; R^1 = H, R^2 = Me; M = Si, Ge;
yield: 30 - 50%]



(ABIBN = Azobisisobutyronitrile)

Mazerolles and Faucher obtained an oxagermabicyclododecane by the dehydrocondensation of 6 - methyl - 6 - germacycloundecan - 1 - ol in the presence of Raney nickel (104). Some of their results are given in Chart 14.

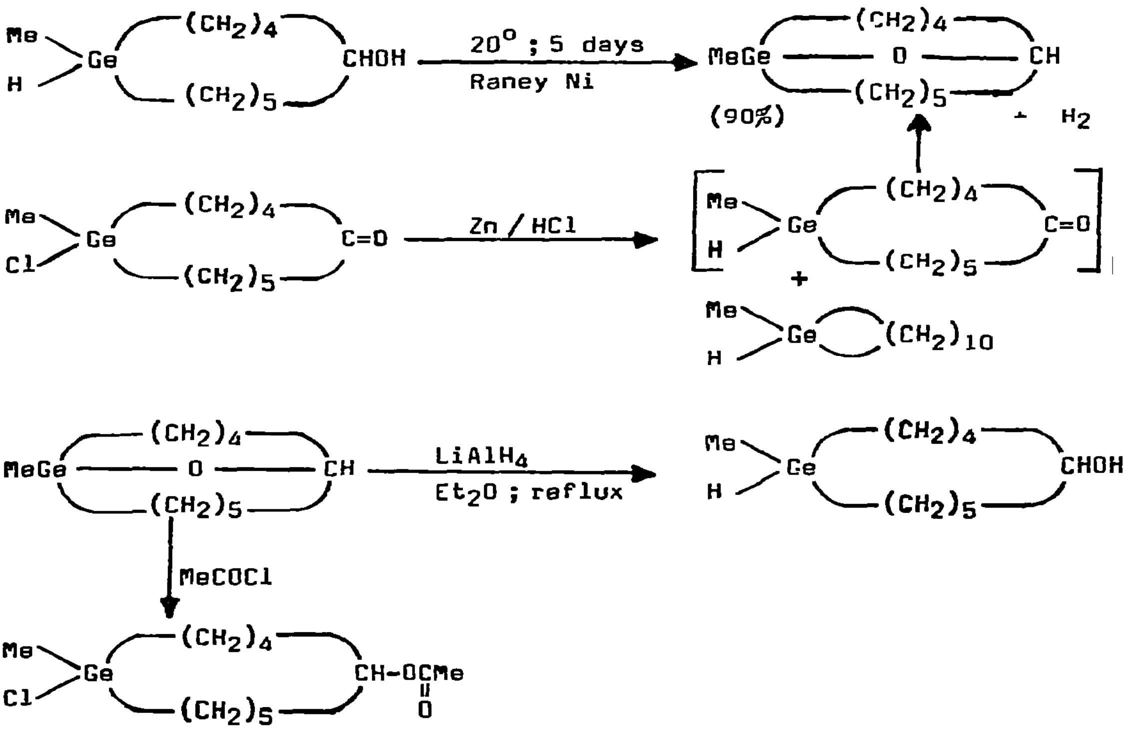


Chart 14. Synthesis and reactions of an oxagermabicyclododecane.

A number of publications regarding the syntheses of oxygen (96, 103 105 - 109), sulfur (96, 106) and nitrogen (96, 106) containing germacyclanes have appeared. Some of the results reported are summarized in Chart 15.

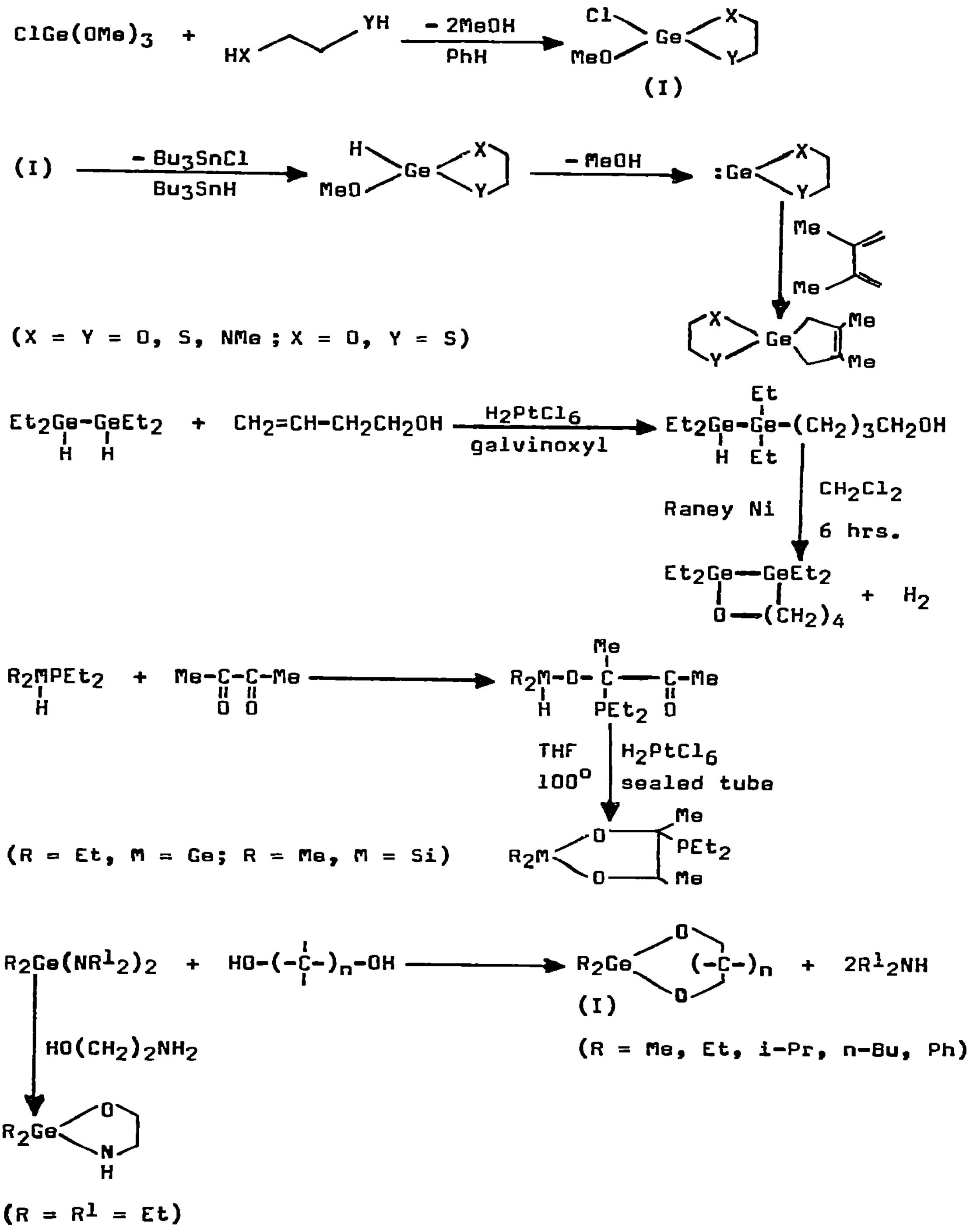
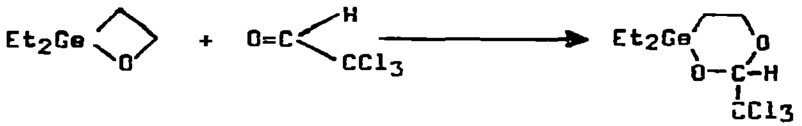
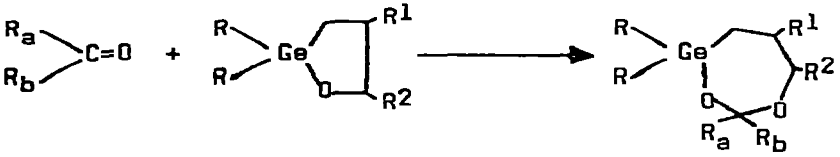


Chart 15. Synthesis of some germacyclanes.

The spectral study (IR and NMR) of compounds of the type (I) has been put forward to demonstrate a dimerization by coordination. The association is disfavoured by the presence of substituents on the cycle and by hindering substituents with donor effect on the germanium (105).

Satgé et al. reported their investigations on the insertion reactions of carbonyl derivatives (e.g. acetaldehyde, chloral, hexachloro- and hexafluoro-acetone) on the metal-oxygen bond of cyclic ethers containing silicon, germanium or tin atoms in the ring (110):

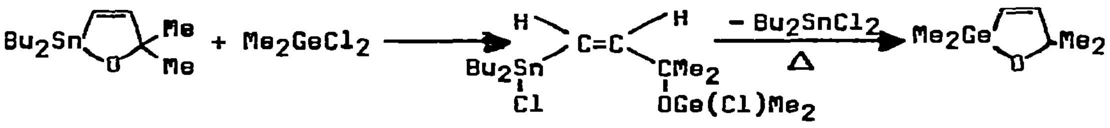




[R = Me, Et, Bu, Ph; R_a = Me, Pr, CCl_3, CF_3;
R_b = H, CF_3; R^1 = H, Me; R^2 = H, Me]

The mechanism of these reactions has been discussed in relation to the nature of carbonyl derivatives and metal heteroatom in the starting cyclic compounds, as well as catalytic and solvent effects.

The preparation of 2, 2, 5, 5 - tetramethyl - 1 - oxa - 2 - germacyclopentene has been accomplished according to the reaction (111, 112):



Carbon - functional germanium compounds

Various addition reactions of hydrogermanes and hydrohalogermanes on unsaturated groups have been used to synthesize triorganogermyl substituted alcohols (108, 109). Some of these reactions are given in Chart 16.

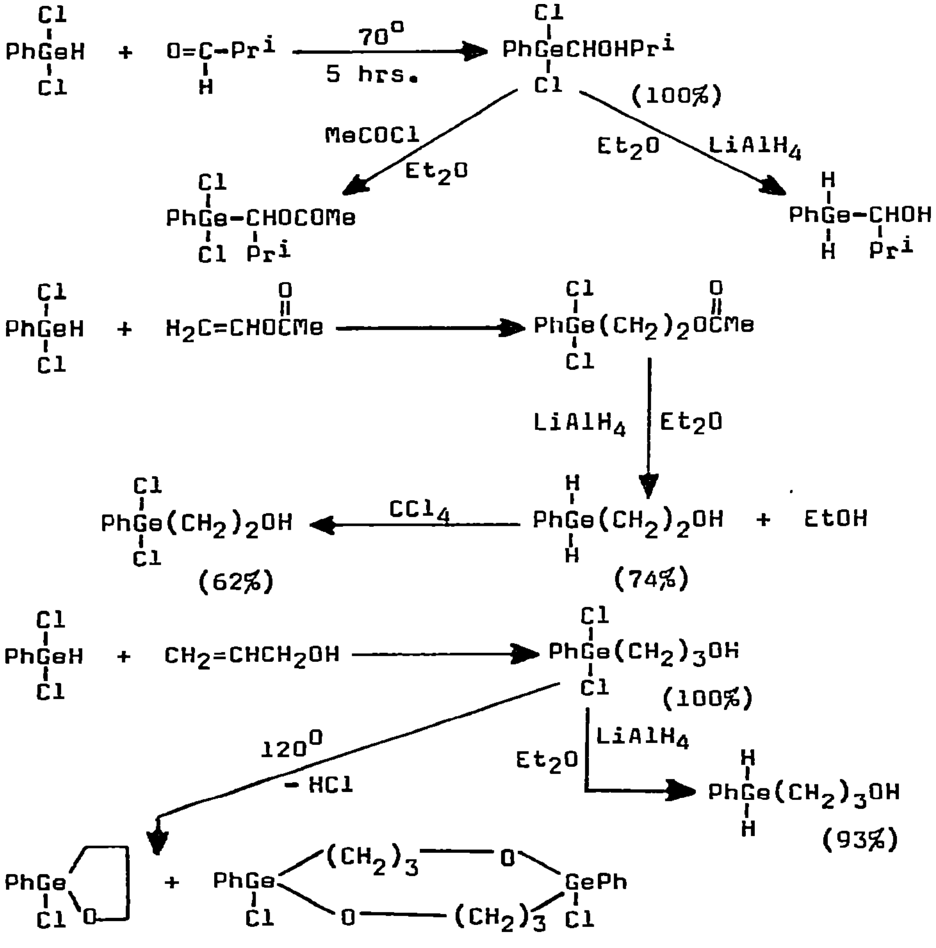


Chart 16. Synthesis and reactions of α, β and γ- phenyl - chlorogermyl alcohols.

Several publications regarding synthesis of a variety of carbon-functional germanium compounds have appeared (113 - 115). Some of these synthetic routes are summarized in Chart 17.

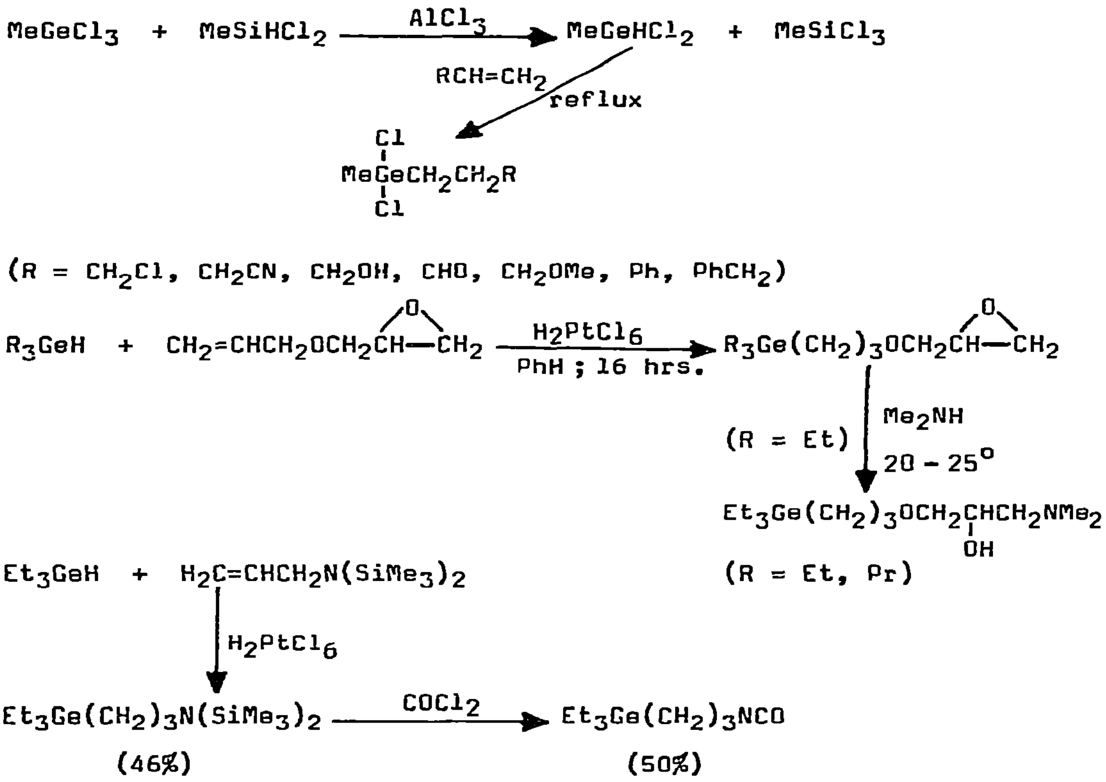
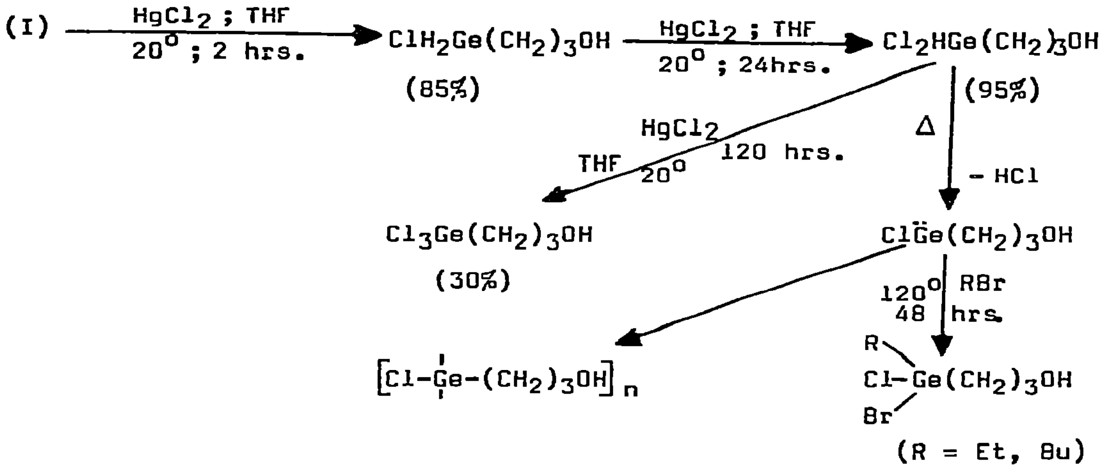


Chart 17. Synthetic routes to some carbon-functional germanium compounds.

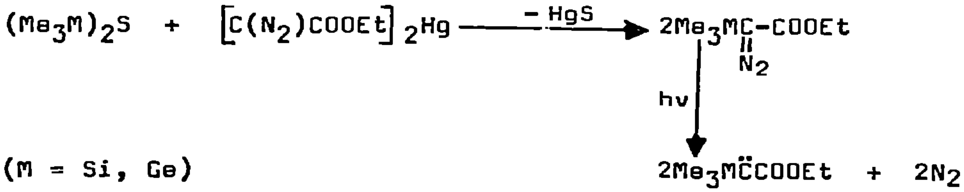
The divalent organogermanium intermediates obtained from decomposition of some hydrogermyl-1-propanols could be used to synthesize other carbon-functional germanium compounds (116):

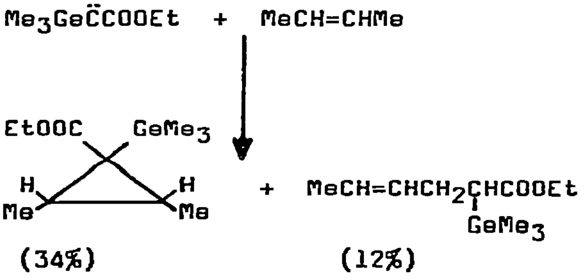
$$Cl_3Ge(CH_2)_2COOH + LiAlH_4 \xrightarrow[-10^\circ]{Et_2O} H_3Ge(CH_2)_3OH$$

(I) (72%)

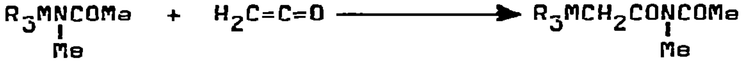


Some diazoacetates containing Group IV B elements have been photolytically cleaved to give carbenes (117). Various insertion reactions of these and others (118) have been reported.





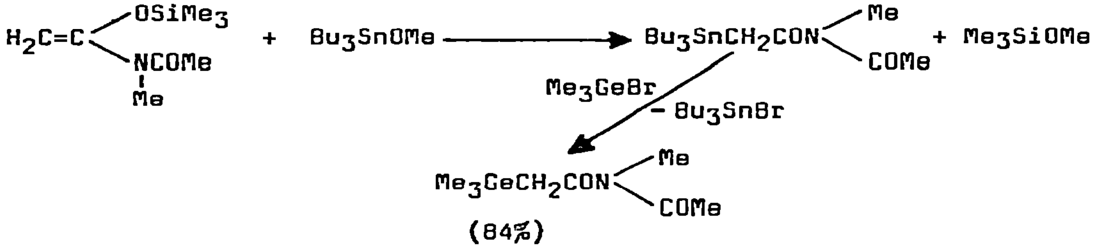
In a study of the reactions of ketene with germylated and stannylated amides, it has been shown that only C-derivatives are formed (in contrast to the silicon analogs where O - derivatives are formed) (119):



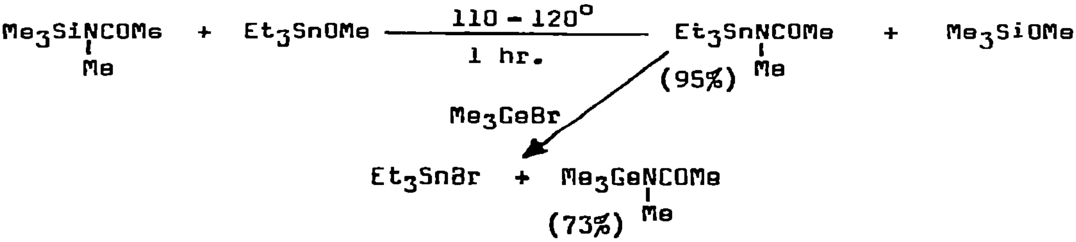
$$R_3M\underset{\displaystyle Me}{N}COMe + H_2C{=}C{=}O \longrightarrow R_3MCH_2CO\underset{\displaystyle Me}{N}COMe$$

(R = Me, Et; M = Ge, Sn)

Also, only C - isomers were isolated when other methods were used for synthesizing germanium and tin containing derivatives of substituted acetamides:



It is interesting to note that above type of exchange reactions can be applied not only for the transfer of keto-enol residue from one Group IV B element to another, but also for the preparation of the N - germyl - and N - stannyl - N - methylacetamides used as starting compounds:

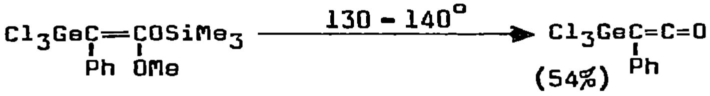


The preparation and reactions of some metalated ketenes have been reported (120 - 122):

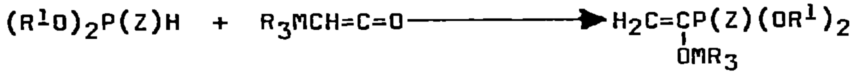
$$R_3MCH_2COOH + H_2C{=}C{=}O \longrightarrow \underset{\displaystyle (I)}{R_3MCH_2COOCOMe}$$

$$(I) \xrightarrow[30-40\ \text{min.}]{140-150^{o}} R_3MCH{=}C{=}O + R_3MCH_2COOH$$

$(R = Me, Et;\ M = Si, Ge)$



$$Cl_3GeC(Ph){=}C(OMe)OSiMe_3 \xrightarrow{130-140^{o}} Cl_3GeC(Ph){=}C{=}O\ (54\%)$$



$$(R^1O)_2P(Z)H + R_3MCH{=}C{=}O \longrightarrow H_2C{=}C(OMR_3)P(Z)(OR^1)_2$$

$[R, R^1, M, Z = Me, Me, Si, O;\ Et, Et, Si, O;\ Me, Me, Si, S$ and $Et, Me, Ge, O]$

Miscellaneous compounds and reactions

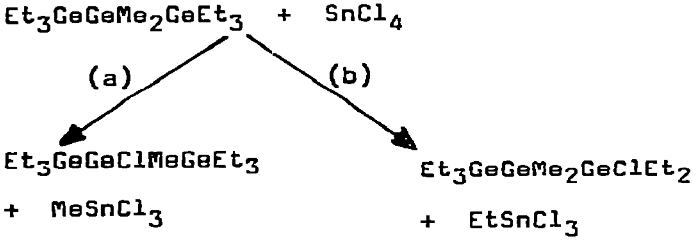
Bulten and Drenth reported their studies on non-catalyzed redistribution reactions of alkylmono- and -polygermanes with germanium- and tin-tetrachlorides (123):

$$R_4M + M^1Cl_4 \longrightarrow R_3MCl + RM^1Cl_3$$

$(M = Ge,\ M^1 = Ge, Sn;\ M = Sn,\ M^1 = Ge)$

$$R_3GeGeR_3 + GeCl_4 \longrightarrow R_3GeGeClR_2 + RGeCl_3$$

$(R = Et, Bu)$



$$Et_3GeGeMe_2GeEt_3 + SnCl_4 \xrightarrow{(a)} Et_3GeGeClMeGeEt_3 + MeSnCl_3$$

$$Et_3GeGeMe_2GeEt_3 + SnCl_4 \xrightarrow{(b)} Et_3GeGeMe_2GeClEt_2 + EtSnCl_3$$

Reaction medium	(a)	(b)
MeCOCl	$>90\%$	$<10\%$
$MeNO_2$	$<5\%$	$>95\%$

$$Et_2PrBuGe + SnCl_4 \xrightarrow{MeNO_2} EtPrBuGeCl + EtSnCl_3$$

(rate of dealkylation being: Me > Et > Pr > Bu)

The high selectivity of these reactions enables the facile preparation of mixed alkyl-substituted mono- and polygermanes. On the basis of observed substituent and solvent effects these reactions are concluded to proceed by an electrophilic substitution at carbon through transition states in which considerable charge separation has occurred.

Some exchange reactions which provide convenient routes to a variety of organogermanes have been reported (119, 124, 125):

$$GeX_4 + R_4Sn \xrightarrow{250^{\circ}} R_2GeX_2 + R_2SnX_2$$

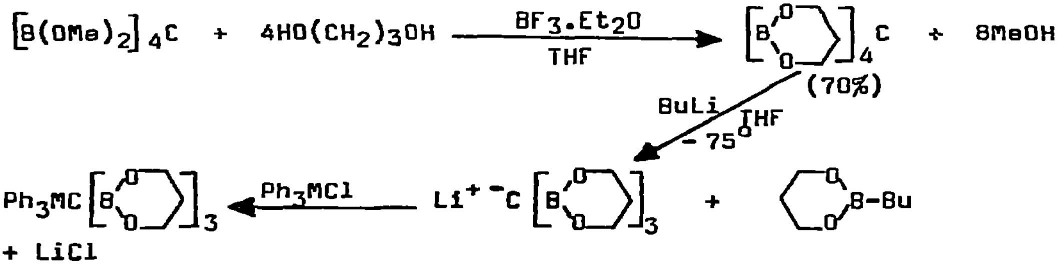
(R = Et, Bu; X = Br, I)

$$Me_3GeBr + Bu_3SnOMe \longrightarrow Me_3GeOMe + Bu_3SnBr$$

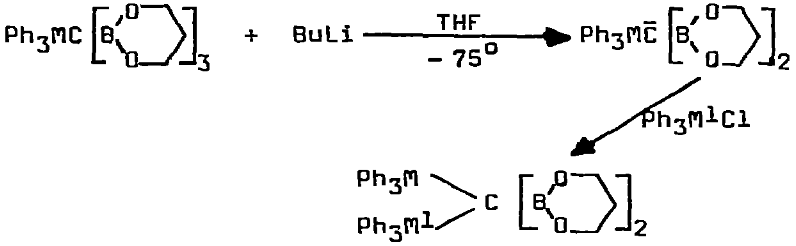
$$2Me_3MX + (Bu_3Sn)_2O \longrightarrow (Me_3M)_2O + 2Bu_3SnX$$

(M = Si, Ge; X = Cl, Br)

Tetrametallomethanes containing one, two or three Group IV B metal atoms and boron (126) and some complexes of the type $Cp_2M(CH_2M^1Me_3)_nCl_{2-n}$ (where Cp = π-C_5H_5; M = Ti, Zr; M^1 = Si, Ge, n = 1 or 2) (127) have been synthesized according to the reactions:



[M = Ge (74%); Sn (70%); Pb (48%)]



($M = M^1 = Sn$; $M = M^1 = Pb$; $M = Sn$, $M^1 = Ge$; $M = Pb$, $M^1 = Ge$ etc)

$$(\pi\text{-}C_5H_5)_2TiCl_2 + 2Me_3GeCH_2Li \xrightarrow{Et_2O} (\pi\text{-}C_5H_5)_2Ti(CH_2GeMe_3)_2 + 2LiCl$$

Physico - chemical investigations

It has been shown that successive halogen substitution in methylgermanium fluorides and chlorides leads to different observed trends in the dipole moments of the various compounds. These trends may be explained in terms of hybridisation and polarisability effects (128). A study of the dipole moments of germanium tetraalkoxides [$Ge(OR)_4$; R = alkyl group] indicated that the hindrance to normal rotation began at R = Bu whereas in $Si(OR)_4$ it began at R = Et. The degree of intermolecular interaction (dipole orientation) increased from $Si(OR)_4$ to $Ge(OR)_4$ (129).

The stepwise solvolysis (as shown by conductivity method) of germanium tetrachloride (130) and conductivities and equivalent conductivities for various chloromethylgermanes in methanol and ethanol (131) have been reported. The strengths of the chloromethylgermanes as acids diminish in the order: $MeGeCl_3 > Me_2GeCl_2 > Me_3GeCl$.

A review on thermochemistry of chemical compounds including enthalpies of formation of organometallic compounds has appeared (132). Zaitsev and Maslov derived certain thermodynamic parameters for germanium halides GeX_4, GeX_3Y and GeX_2YZ (where X, Y, Z = F, Cl, Br, I, H) (133) and also calculated the heat capacities of $RGeH_3$ (where R = C_2D_5, PH_2, AsD_2) (134). The heats of evaporation, parachor, surface tension etc. of a series of covalent hydrides (135); specific heats and phase transitions for derivatives of the type Et_4M (where M = Si, Ge, Sn) (136) and surface tension data for a variety of organometallic compounds (141) have been reported. The primary process in the mercury photosensitized decomposition of tetramethylgermane has been shown to involve a C - H bond cleavage and the atomic cracking occurs at high intensities giving methyl radicals (137). The vacuum-ultrviolet photolysis (138) and the pyrolysis (139) of germane produced significant concentrations of several reactive species. A study of the pyrolysis of some compounds of the type $Ph_3MOOC(Me_2)Ph$ (where M = Si, Ge, Sn, Pb) indicated the thermal stability to decline in the order: Ge $>$ Si $>$ Sn $>$ Pb (140).

The observed order of acidity (Si $\geqslant$ Ge $>$ C) for compounds of the type R_3MCOOH (where R = Me, Ph, M = C, Si, Ge; R = H, M = C, Ge) has been explained in terms of the larger sizes and polarizabilities of silicon and germanium relative to carbon (142, 143). The pK values of a series of monosubstituted acetylenes of the type $R_3M{-}C{\equiv}CH$ (where R = Me, Et; M = C, Si, Ge, Sn) show that the presence of Group IV elements at the triple bond is accompanied by an increase in proton mobility of the $\equiv$C-H bond compared with alkylacetylenes (144). The rate constants of trimethylgermyl - substituted alcohols $[Me_3Ge(CH_2)_nOH$ where n = 1 - 4$]$ invariably decrease with the increasing 'n' (145). Sakurai et al. reported the formation of a charge - transfer complex of hexamethyldigermane with tetracyanoethylene (146).

Stereochemistry of some complexes of Group IV B elements has been reviewed (147, 148). Eaborn and coworkers continued their investigations (see AS 72 ; p.266) on the optically active germanecarboxylic acid $(-)R'_3GeCO_2H$ and discussed the stereochemistry of the conversion (149):

$$2(-)\text{-}R'_3GeCO_2H \xrightarrow{200^{o}\ ;\ 10\ \text{min.}} (-)\text{-}R'_3GeCO_2GeR'_3 \quad + \quad CO$$

$$\left[R'_3Ge = Et(1\text{-}C_{10}H_7)PhGe\right]$$

Some reactions of asymmetric silyl- and germyllithiums have been reported (150, 151):

$$R_3MH \quad + \quad BuLi \longrightarrow R_3MLi \xrightarrow{R_3MCl} R_3M\text{-}MR_3$$

$$\left[R_3 = Me(\alpha\text{-}C_{10}H_7)Ph;\ M = Si,\ Ge\right]$$

$$\begin{tikzcd} R_3Ge^{*}Li \quad + \quad ClCH_2COOR^1 \arrow[r] & R_3Ge^{*}CH_2COOR^1 \arrow[d, "LiAlH_4"] \\ & R_3Ge^{*}CH_2CH_2OH \end{tikzcd}$$

$$\left[R_3 = Me(1\text{-}C_{10}H_7)Ph;\ R^1 = Me,\ Et\right]$$

The radiochemistry (152) and the radiochemical transformations and rearrangements in organometallic compounds (153) have been reviewed. The radioactive tracers have been used to study the equilibrium distribution of microamounts of hydrocarbon, methylgermane, hydrogen sulfide and arsine in monogermane between the liquid and vapour phase (154).

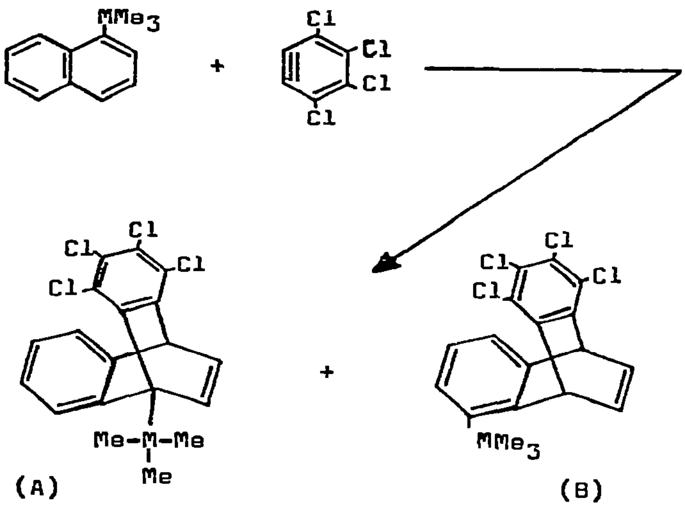
The magnitude of the effect of metal on the π-electron system of $PhMR_3$ (where M = Si, Ge, Sn, C; R = H, Me) decreased in the stated order of M and R (155). A comparative study of direct and across-space $(p-d)\pi$ bonding interactions in some selected Group IV compounds has been the subject of a Ph.D. thesis (156). The perturbational molecular orbital treatment of hyperconjugation in conjunction with CNDO/2 calculations, has been applied to rationalize trends in a number of experimental properties of compounds of C, Si, Ge and Sn (157). The theoretical evidence for $\sigma-\pi$ conjugation in compounds of the type $Me_3MCH_2CH{=}CH_2$ (where M = C, Si, Ge, Sn, Pb) (158) and the conformational consequences of hyperconjugation in β - silyl- and β- germylethyl cations and anions have been presented (159).

Dessy and Bares presented a broad survey of organometallic electrochemistry where special attention has been given to (a) the available pathways in organometallic electrochemical reactions, and (b) the physical consequences of the addition (or abstraction) of an electron from an organometallic molecule (160). The electrochemistry of triphenylgermanium halides (Ph_3GeX where X = F, Cl, Br, I) in 1, 2 - dimethoxyethane (DME) has been investigated. The results indicated the reduction of chloride and bromide to be irreversible single - electron processes resulting in the formation of a germyl radical (161):

$$\begin{tikzcd}
Ph_3GeX \arrow[rr, "e"] & & Ph_3Ge^{\bullet} + X^{-} \quad (X = Cl,\ Br) \arrow[dl, "\text{dimerization}"'] \arrow[dr, "\text{DME}"] & & \\
 & (Ph_3Ge)_2 & & Ph_3GeH \arrow[dr, "\text{peroxide*}"] & \\
H_2O + (Ph_3Ge)_2O & & & & Ph_3GeOH \arrow[llll]
\end{tikzcd}$$

(* arising from the autoxidation of DME when exposed to air)

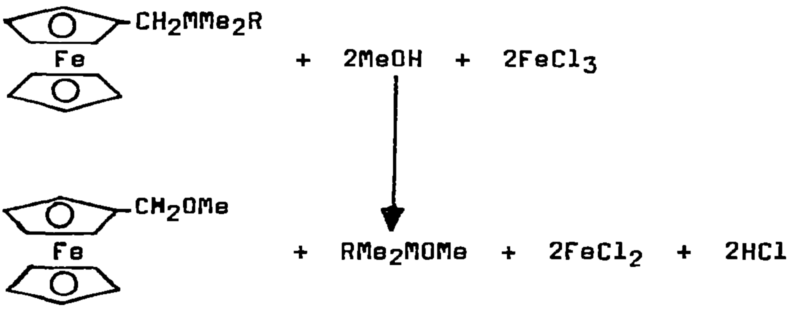
The addition of tetrachlorobenzyne to organometal substituted naphthalene has been shown to proceed as (162):



(M = C, Si, Ge, Sn)

Using NMR spectroscopy to study the rotation about the carbon - Group IV B element single bond (in adduct A) the authors observed the decrease in the rotational barrier on increasing the atomic size.

Yamamoto et al. continued their studies on the solvolysis of the metal - carbon bond (see AS 72 ; p.266) of ferrocenylmethyl derivatives of silicon and germanium (163):



(R = Me, Et, i-Pr etc.; M = Si, Ge)

and interpreted the observed higher reactivity of the germanium derivative relative to the silicon one in terms of a possible change in the transition state depending on the nature of the leaving group.

Some general articles on substitution, isomerization etc. of organometallic compounds have appeared (164 - 170).

Some other studies include: kinetics of the thermal decomposition of peroxides of the type $Ph_3GeOOSiR_3$ (where R = Et, Pr, Bu, Ph) (171); multiple - scattering X_α study of silane and germane (172); calculation of ground state energies for molecules of the type MH_4 (where M = C, Si, Ge, Sn, Pb) (173); polarographic behaviour of some Group IV B derivatives of naphthalene (174); mechanism of α- effect in α- carbofunctional organic compounds of Group IV B elements (175); calculation of force fields, frequencies and the centrifugal distortion constants for compounds of the type H_3GeX (where X = Me, $C{\equiv}N$, $C{\equiv}CH$) and their deuterated derivatives (176); liquid-phase oxidation of germanium - mercury bonded derivatives (177); relative rates of germylene and silylene insertion into alkylgermanes (178); product studies on reactions of recoiling germanium atoms in germane, digermane and germane - silane mixtures (179); reaction of alkyl derivatives of Group IV B elements with Ph_3CBr (180) and base strengths of compounds of the general formula $H_3M(CH_2)_nOMe$ (where M = Si, Ge; n = 2, 3, 4, 6) (181).

Spectral studies

A number of publications on the spectral investigations of organogermanium compounds have appeared.

IR and Raman studies

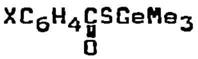
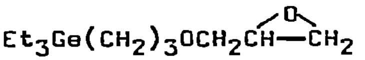
A review article on the infrared and Raman spectra of inorganic and organometallic compounds has appeared (182). According to the data of IR and PMR spectra, in organosilicon and organogermanium compounds containing unlike substituents, the degree of $d_\pi - p_\pi$ interaction is not the sum of the contributions of the individual substituents but is determined by the nature of the latter (183). Infrared spectroscopy has been used to investigate the relative basicities and the effects of $d_{\pi}-p_{\pi}$ interaction of various oxygermanes (184) and peroxides of the type $Ph_3GeOOSiR_3$ (where R = Me, Bu, Ph etc.) (185).

On the basis of Raman and infrared spectra under various conditions, together with the observed depolarization values, it has been possible to make a new vibrational assignment for the molecules of the type $X_3MCo(CO)_4$ (where M = Si, Ge, Sn; X = Cl, Br, I) (186). Onaka reported the infrared absorption spectra (2200 - 50 cm^{-1}) for molecules of the type $X_3MMn(CO)_5$ (where M = Si, Ge, Sn; X = Cl, Br, I). The metal - metal stretching force constant varies with the halogen atom, and increases as the electronegativity of X increases. The force constant depends also on the Group IV B atom, and increases in the order of: Si-Mn $\geqslant$ Ge-Mn $>$ Sn-Mn (187).

The perturbation theory treatment of Overend and Scherer has been applied to compounds of the type R_3MCOR^1 or R_3MCOMR_3 (where R, R^1 = alkyl or aryl). The results show α- metal CO electronic interactions to be of similar magnitude for C, Ge and Sn. The ν(CO) values for the series Ph_3MCOMe suggest, not surprisingly, that $(d-p)_{\pi}$ bonding is less important for Ge and Sn than for Si (188). Guillory and coworkers reported the use of Fourier transform spectroscopy for obtaining far infrared spectra of matrix - isolated species (189, 190).

Rosenberg and Ozier used standard far infrared equipment to make accurate frequency measurements of the pure rotational lines in GeH_4 (191). The normal vibrations of some methylhydro - silanes and - germanes have been calculated using the force constants obtained from the modified Urey - Bradley force field treatment of the observed vibrational frequencies (192). Some mixed halides of the type Cl_3GeBr, Cl_2GeBr_2 etc. (193) and hydrohalides of the type

$HGeBrI_2$, $HGeBr_2I$ etc. (27) have been identified by Raman spectroscopy in various halogen - exchange reactions. Haszeldine et al. used infrared spectroscopy of several Group IV B element substituted transition metal complexes to study the trans-influence of substituted silyl, germyl and stannyl groups (194). Other studies and articles include: mechanism of methoxyphenyl-carbene insertion into Group IV B element - hydrogen bond (32, 33) (see also p.8); facile and reversible homolysis of Fe - Ge bonds by Lewis bases (62); calculation of electrooptical parameters and absolute intensities in Raman spectra of some methylchlorogermanes (195); IR spectroscopic study of the reactions of silica - germania absorbents (196) and Raman radial mode of gaseous germacyclopentane (197). More specific studies include the following compounds:

$(\pi-C_5H_5)_2Ge$ (18, 19); germylcyclopentadienes and germylindene (198); $(Me_3CCH_2)_4Ge$ (22); MX_4 (M = C, Si, Ge, Sn etc.; X = F, Cl, Br, I) (199); $XCH_2YH_3(-D_3)$ (X = Cl, Br; Y = Si, Ge) (200); GeD_4 (201); GeH_4 (202); Me_4M (M = C, Si, Ge etc.) (203); $[(C_6F_5)_3Ge]_2Cd.2L$ ($L = Ph_3P$, Et_2NH etc.) (40); $3\text{-}Ge\text{-}1,7\text{-}B_9C_2H_{11}$ (52); $1,2,3,\text{-}GeB_9H_9CHE$ (E = P, As) (53); $(C_5H_5)_2TiGePh_3$ (55); $Me_3MMn(CO)_5$ (M = Si, Ge, Sn) (204); $(CO)_5MSb(M^1Me_3)_3$ (M = Cr, Mo, W; M^1 = Ge, Sn) (57); $(CO)_5MTe(M^1Me_3)_2$ (M = Cr, Mo, W; M^1 = Ge, Sn, Pb) (58); $Ph_2GeMn(CO)_4COMe$ (60) (see also p. 20); $H_3GeRe(CO)_5$ (61); $(C_5H_5)Fe(CO)_2MX_2Ni(CO)(C_5H_5)$ (M = Ge, Sn; X = Cl, Br) (63); vinyl - substituted germanium derivatives of transition metal carbonyls (64, 65) (see also p.22); $\pi-C_5H_5(R_3Ge)(L)Ni$ ($R_3Ge = Cl_3Ge$, Ph_3Ge, Br_3Ge; $L = Et_3P$, Ph_3P etc.) (66); $Os(CO)_4X_2$ (X = Me, H_3Ge, Ph_3Sn, Me_3Pb etc.) (67); $H_3GeXIr(CO)Cl(PPh_3)_2$ (X = Cl, Br, I) (68); germylhydrazines and germyldiazenes (69); germanium phosphinimines (70); $Me_{4-n}M[N{=}C(CF_3)_2]_n$ (M = Si, Ge, Sn; n = 1 - 4) (73); $Me_3MQ(CF_3)_2$ (M = Si, Ge, Sn; Q = P, As) (76); secondary germanium - arsines and mixed Ge – Sn arsines (79); Me_3GeO_2SMe (205); $R_3MOOM^1R^1_3$ (R = Me, Ph; R^1 = Me, Et, Bu, Ph; M, M^1 = Si, Ge) (206); tributylgermanium oximates (80); cyclic germanium 1,4-cyclohexanediolates (81); germoboroxanes (83);  $XC_6H_4\underset{O}{\underset{\|}{C}}SGeMe_3$ (X = p-NO_2, m-Cl, p-Me etc.) (85);  $R\underset{S}{\underset{\|}{C}}SMMe_3$ (R = alkyl, aryl; M = Si, Ge, Sn) (86); $Me_{4-n}M(SeMe)_n$ (M = Si, Ge, Sn; n = 1 – 4) (87); triethylgermyl – substituted dihydrofurans (89); $Ph_2M(C{\equiv}C{-}C{\equiv}CH)_2$ (94); $Me_3MC{\equiv}C{-}C{\equiv}CMMe_3$ (M = C, Si, Ge) (95); germanium acetylide (207); germacyclanes (96, 103 – 105, 111);  $Et_3Ge(CH_2)_3OCH_2\overset{O}{CH{-}CH_2}$ (114); $(C_5H_5)_2Ti(CH_2GeMe_3)_2$ (127); R_3MCOOH (R = H, Me, Ph; M = C, Si, Ge) (142, 143); $H_3M(CH_2)_nOMe$ (M = Si, Ge; n = 2,3,4,6) (181); pseudohalo(methyl)germanes (208); and some germanium complexes (209 – 211).

NMR studies

Satgé and coworkers used NMR spectroscopy to characterize the products formed in various reactions of divalent organogermanium intermediates (96, 103, 116). In the compounds of the type MeH_2GeX and $MeGeX_3$ (where X = CN, NCS, NCO) the NMR evidence strongly favours Ge – N bonding in – NCO and – NCS derivatives which is supported by vibrational spectra. For the cyanides the NMR evidence suggested a carbon – bonded CN group with just a possibility of some isocyanide also being present (208). The integrated absorpotion coefficient of the $C{\equiv}C$ and acetylenic CH valence vibrations varied linearly with the acetylenic proton NMR chemical shift (at infinite dilution in CCl_4) in a series of $R_3MC{\equiv}CH$ compounds (where R = Me, Ph; M = C, Si, Ge, Sn, Pb) (212). However, no simple relation between the ^{13}C-NMR shifts of the acetylenic carbon and the IR data was found. The results are interpreted in terms of $(d-p)\pi$ effect involving vacant d orbitals of M and the π electrons of the triple bond. Job and Curtis studied the photochemistry of a number of germanium compounds and used NMR spectroscopy to characterize various reaction products (64, 65). The ratio of various isomers in the reactions of organogermanium amides with ketene (119), germylphosphines with ketene and α-diketones (74, 107) and hydrogermylation of naphthyl-containing ditertiary acetylenic γ-glycols (89) has been determined using NMR spectroscopy. The ^{55}Mn-NMR spectra of compounds of the type $R_3MMn(CO)_5$ (where R = Cl, Ph, C_6F_5; M = Si, Ge, Sn) have been studied (213). The large range of chemical shifts is attributed to increasing σ-donor ability of the ligands in the order: $GeCl_3 < SnCl_3 < Ge(C_6F_5)_3 < SnCl_2Ph$ etc. The mechanism and stereochemistry of addition of germylamines to the esters of acetylene dicarboxylic acid (71) and various reactions of germacyclopentenes (98) have been studied using NMR spectroscopy. Other studies and articles include: spin delocalization of Group IV B elements in organic compounds (214); variable temperature ^{1}H-NMR spectroscopy of some germylcyclopentadienes (198); germanotropic equilibrium (215); NMR spectra of propargylic and allenic derivatives of Group IV B elements (216); restricted rotation about the carbon-Group IV B element single bond (162); C_6H_6 vs. C_6F_6 induced solvent shifts in PMR spectra of methyl derivatives of Group IV B elements (217); ^{13}C-NMR chemical shifts of methyl groups in the compounds of the type Me_3MSPh (where M = C, Si, Ge, Sn, Pb) (218); ^{73}Ge-NMR spectra of GeX_4 (where X = Cl, Br, I) (219); ^{14}N-NMR spectra of the alkyl-element-azides (element = B, Al, Tl, C, Si, Ge, Sn, Pb, As) (220); phase transitions in solid germane (221) and ^{11}B-NMR spectra of some phosphagerma- and arsagermacarboranes (53). More specific studies include the following compounds: $(\pi-C_5H_5)_2Ge$ (18); tetra-1-adamantyl-germane (21); $(Me_3CCH_2)_4Ge$ (22); $R_3MCHXC_6H_4Y$ [where R = alkyl, Ph; M = Si, Ge, Sn; X = OMe, NC_nH_{2n} (n = 2, 4) and Y = p-OMe, p-Me, p-Cl, H] (33); 3-Ge-1,7-$B_9C_2H_{11}$ (52);

$Ph_2GeMn(CO)_4COMe$ (60); $(C_5H_5)Fe(CO)_2MX_2Ni(CO)(C_5H_5)$ (where M = Ge, Sn; X = Cl, Br) (63); π-$C_5H_5(R_3Ge)(L)Ni$ (where R_3Ge = Cl_3Ge, Br_3Ge, Ph_3Ge; L = Ph_3P etc.) (66); $Os(CO)_4X_2$ (where X = Me, H_3Ge, Ph_3Sn, Me_3Pb etc.) (67); $H_3GeYIr(CO)Cl(PPh_3)_2$ (where Y = Cl, Br, I) (68); germylhydrazines and germyldiazenes (69); $Me_{4-n}M[N{=}C(CF_3)_2]_n$ (where M = Si, Ge, Sn; n = 1 – 4) (73); $Me_3MQ(CF_3)_2$ (where M = Si, Ge, Sn; Q = P, As) (76); Ge – As bonded compounds (79); germanium – transition metal complexes (57, 58); some Ge – S (85, 86) and Ge – Se derivatives (87); compounds containing heterocyclic germanium (97, 99, 101, 104, 105, 108, 110); α, β and γ - phenylchlorogermyl alcohols (109); carbon - functional germanium compounds (113, 114, 143, 181); tetrametallomethanes containing Group IV B elements and boron (126); $(C_5H_5)_2Ti(CH_2GeMe_3)_2$ (127) and mixed halides of the type $Cl_3Si(CH_2)_nGeCl_3$ (where n = 1, 2, 3), $(XMe_2SiCH_2)_2GeCl_2$ (where X = F, OMe, $OSiMe_3$, H) etc. (15).

Miscellaneous

The characterization of organometallic radicals by ESR spectroscopy has been reviewed (222, 223). The ESR spectrum of a series of allyl radicals ($\dot{C}H_2CH{=}CHCH_2MR_3$, where MR_3 = Me_3Ge, Me_3Si, Bu_3Sn etc.) show a temperature - dependent variation of the hyperfine splitting constants. These radicals exhibit a barrier to hindered internal rotation which increases with atomic number (224). Bennett and Howard reported the radical stabilities of some peroxy radicals to decrease in the order $Me_3PbOO^\bullet > Me_3SnOO^\bullet > Me_3SiOO^\bullet$ with the position of $Me_3GeOO^\bullet$ in some doubt (225). The study has been made (by means of ESR spectroscopy) of the structures of some C, Si, Ge, Sn containing methyl and chloro radicals ($^\bullet MMe_3$ or $^\bullet MCl_3$) (226). The trichloro radicals have been found to be more nonplanar than the trimethyl radicals. The spin delocalization of Group IV B elements in organic compounds was studied by determining the NMR and ESR data for the nitrosyls $Me_3XC_6H_4N(\dot{O})CMe_3$ (where X = C, Si, Ge, Sn, Pb). The spin transfer mechanisms at X in rehybridization were discussed in terms of resonance structures and symmetry change without considering $(p-d)\pi$ delocalization (214). The radical-anions, $Ph_3M\overset{..}{\bar{C}}H\text{-}\dot{C}H_2$ (93), the radical cations of p-trimethylorganometal-N,N-dimethylaniline (227) and the addition of organo-silyl, -germyl and -stannyl radicals to cyclopentadiene (228) have been investigated by ESR spectroscopy. West and Boudjouk reported the ESR spectroscopic data for some organo-silyl and -germyl nitroxides (229).

Mass spectrometry of inorganic and organometallic compounds (including those of germanium) has been the subject of a monograph (230) and four review articles (231-234). Ion-molecule reactions occurring in ionized monogermane have been studied by high-pressure mass spectrometry and rate constants for second- and third-order reactions of all primary ions have been measured. As expected the reactions observed and the specific reaction rates are much more similar to those occurring in monosilane than to those occurring in methane (235). Miller and coworkers reported the mass spectra of compounds of the type $R_3MXC_6F_5$ (where R = Me, Ph; M = Si, Ge, Sn; X = O, S). It has been shown that sulfur and oxygen compounds undergo fewer rearrangements leading to the formation of metal fluorides than do simple pentafluorophenyl derivatives (236). Mass spectroscopic data have been reported for the following compounds: $(\pi-C_5H_5)_2Ge$ (18); alkylgermanes (237, 238); germylcyclopentadienes (198); organogermanium esters and oxides (50); Ge-B bonded compounds (52, 53); $Ph_2GeMn(CO)_4COMe$ (60); $H_3GeRe(CO)_5$ (61); Ge-Ni complexes (63, 66); $Me_3MMn(CO)_5$ (M = Si, Ge, Sn) (204); Me_3GeO_2SMe (205); germacyclanes (81, 99, 101, 104, 239); $R_3MCHXC_6H_4Y$ (R = alkyl, Ph; M = Si, Ge, Sn; X = OMe and Y = p-OMe, p-Me etc.) (33) and pseudohalo(methyl)germanes (208).

The photoelectron spectra of Me_4M (M = C, Si, Ge, Sn, Pb) (240), vinyl- and allylgermanes (241) and $H_3M^1M(CO)_n$ (M^1 = Si, Ge, M = Mn, Re for n = 5; M = Co for n = 4) (242) have been reported. Jolly and Perry used X-ray photoelectron spectroscopy to assess 'd' orbital participation in compounds of silicon and germanium. The results indicate relatively strong $p_\pi - d_\pi$ bonding in the tetramethyl derivatives and the tetrahalides of both silicon and germanium (243). The bonding energies for some related Ge, Sn and Pb compounds have been determined by X-ray photoelectron spectroscopy (244).

The subject of microwave spectroscopy of organometallic and inorganic compounds has been reviewed (245). The microwave spectroscopic measurements have been made on H_3GeNCO (246), H_3GeBr (247), Me_3GeBr (248) and $MeGeH_2F$ (249). Some other studies and articles include: UV data for germyldiazenes (69), $Me_{4-n}M[N{=}C(CF_3)_2]_n$ (M = Si, Ge, Sn; n = 1-4) (73), $XC_6H_4\underset{\underset{O}{\|}}{C}SGeMe_3$ (X = p-NO_2, m-Cl etc.) (85) and $R\underset{\underset{S}{\|}}{C}SMMe_3$ (R = alkyl or aryl; M = Si, Ge, Sn) (86); NQR spectra of Group IV B organometallic halides (250); spin-rotation constants for the hydrogen or fluorine nuclei in compounds of the type MH_4 and MF_4 (M = C, Si, Ge) (251); the rotational spectrum of GeH_4 (252) and Me_3GeH (253); electronic spectra of some organogermanium complexes (254); CH-valence vibrations of compounds of the type Me_4M (M = C, Si, Ge, Sn, Pb) (255) and X-ray-photoemission-spectroscopy molecular-orbital spectra of methane, silane and germane (256).

Various investigations of crystal structures in U.S.S.R. have been reviewed (257). The reports regarding structural data for various organogermanium compounds include: X-ray diffraction study of $(Ph_3Ge)_2O$ (258) (Fig.1); crystal structure of $(C_6F_5)_4Ge$ (259); electron diffraction study of the molecular structure of

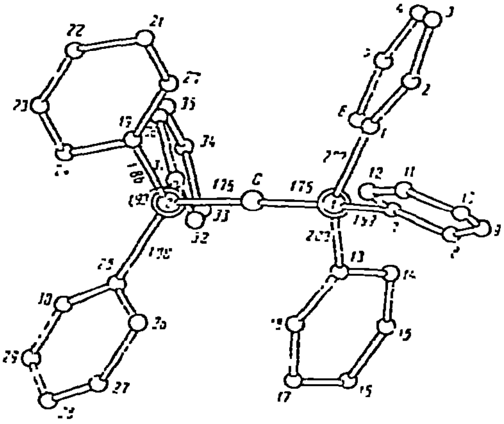


Fig. 1. Geometry of the molecule $(Ph_3Ge)_2O$ [from L.G. Kuz'mina and Yu. T. Struchkov: Zh. Strukt. Khim., 13 (1972) 885.]

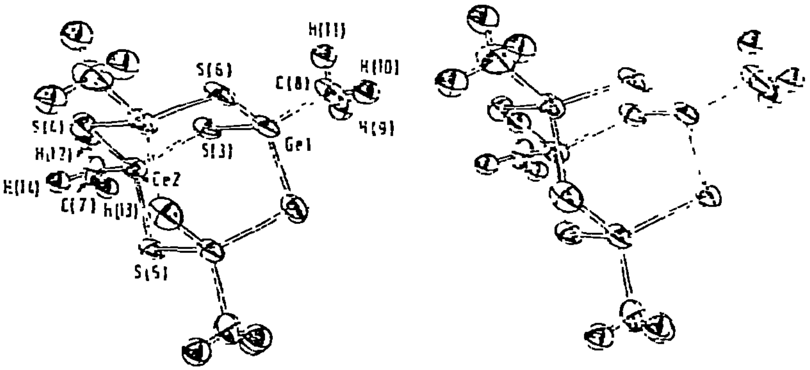


Fig. 2. Stereoscopic view of $(MeGe)_4S_6$ showing the atom numbering system used; S(5) and S(6) lie on a crystallographic two-fold axis [from R.H. Benno and C.J. Fritchie; J. Chem. Soc. Dalton Trans., (1973) 543.]

bis(trimethylgermyl)ketene (260); crystal and molecular structure of $(Me_4N)_3Pt(GeCl_3)_5$ (261); unit-cell data for phenyl(triphenylgermyl)diazomethane (262); X-ray crystallography of $Ru_2(CO)_4C_8H_6(GeMe_3)_2$ (263) and $(MeGe)_4S_6$ (264) (Fig.2)

Analysis and applications

The use of gas chromatography for inorganic and organometallic compounds (including those of germanium) has been the subject of a book (265) and a review article (266). It has been shown that organometallic derivatives of the series Et_3MH and Et_4M (M = Si, Ge, Sn) can be separated by the methods of gas adsorption and gas-liquid chromatography. The values of the absolute retainable volumes, heats of adsorption, and dissolution of the indicated compounds on adsorbents and solvents of different types were measured (267).

Various claims regarding applications of organogermanium compounds include: carboxylethyl germanium sesquioxide in the treatment of hypertonia (268); tetravalent germanium compounds as polymerization catalysts (269); methylgermanium trichloride as a stabilizer to prevent the discoloration of maleic anhydride at elevated temperatures (270); germanium-acetylenic derivatives as high-resistance semiconductors (94) and tetramethylammonium salts of the MCl^-_3 (M = Ge, Sn) anions as convenient solvents for some homogeneous catalytic reactions of olefins (271).

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