GERMANIUM

ANNUAL SURVEY COVERING THE YEAR 1974

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CONTENTS

Germanium, Annual Survey covering the year 1973 see J. Organometal. Chem., 89 (1975) 1-80.

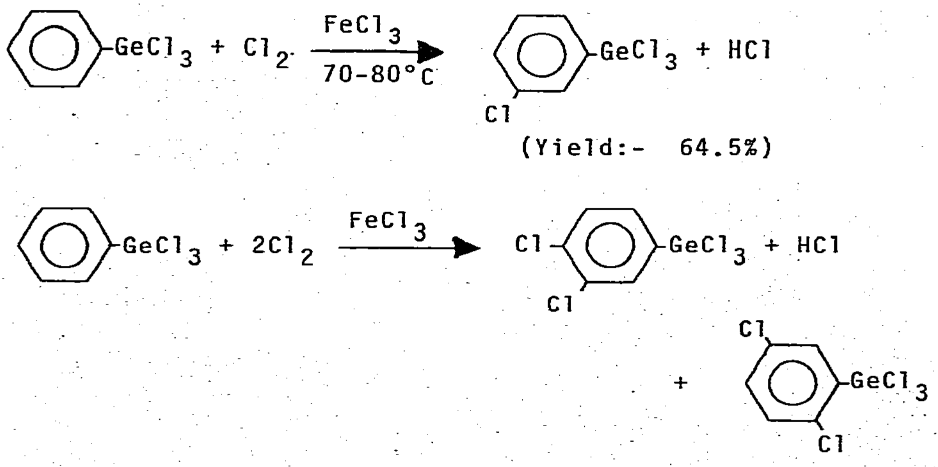
Books and reviews

Apart from the Annual Survey covering the year 1972 (1), a new series entitled Annual Reports in Inorganic and General Syntheses has started (2,3). The purpose of the series is the organization and summary of recent syntheses in inorganic and, in part, organometallic chemistry. Various aspects of radicals containing Group IVB elements have been reviewed (4,5). The literature on inorganic, organic and organometallic compounds containing elements of Group IVB for the years 1973 and 1974 has been surveyed (6-8). Few other articles (9-13) which cover broad aspects of organogermanium chemistry have appeared.

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

Germanium-halogen compounds

The electrophilic halogenation of phenyltrichlorogermane has been used to synthesize phenyltrichlorogermanes of the type $X_nC_6H_{5-n}GeCl_3$ (X = Cl, Br; n = 1,2). The reaction has been shown to proceed in accordance with the following scheme (14):

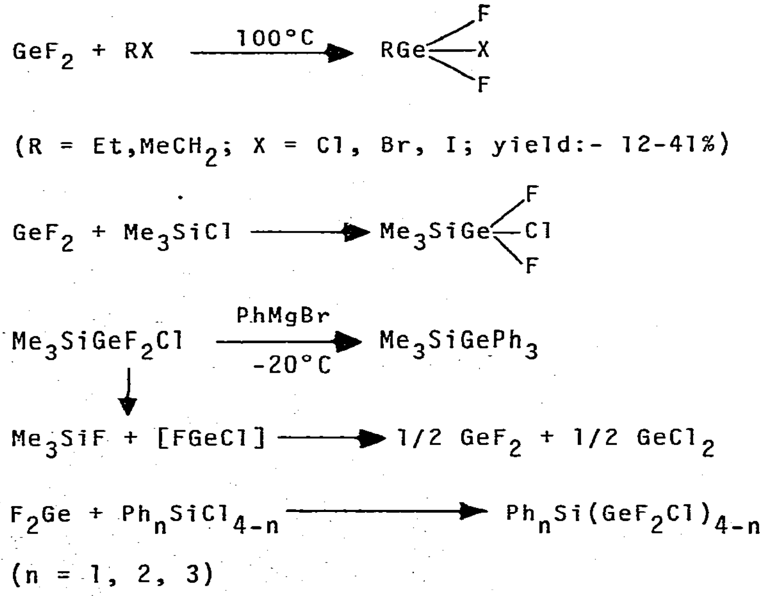


Thus the trichlorogermyl group orients a chlorine atom entering the aromatic nucleus into the meta position. On further chlorination of trichloro(chlorophenyl)germane the orienting influence of the chlorine atom is predominant. Attempts to prepare a derivative trichlorinated to the nucleus resulted in carbon-germanium bond cleavage which has been shown to be more marked for phenyltrichlorogermane than for phenyltrichlorosilane under analogous conditions. The cleavage of carbon-germanium bond has been reported to occur in the radical chlorination of phenyltrichlorogermane:

$$C_6H_5GeCl_3 + Cl_2 \xrightarrow[5\text{-}10°C]{UV} C_6H_5Cl + GeCl_4$$

$$C_6H_5Cl + 3Cl_2 \xrightarrow{UV} C_6H_5Cl_7$$

Satgé et al. reported their investigations on the insertion reactions of difluorogermylene (:GeF_2) into a variety of bonds (15). Some of their results are compiled in Chart 1.



$$GeF_2 + RX \xrightarrow{100°C} RGeF_2X$$

(R = Et,$MeCH_2$; X = Cl, Br, I; yield:- 12-41%)

$$GeF_2 + Me_3SiCl \longrightarrow Me_3SiGeF_2Cl$$

$$Me_3SiGeF_2Cl \xrightarrow[-20°C]{PhMgBr} Me_3SiGePh_3$$

$$\downarrow$$

$$Me_3SiF + [FGeCl] \longrightarrow 1/2\ GeF_2 + 1/2\ GeCl_2$$

$$F_2Ge + Ph_nSiCl_{4-n} \longrightarrow Ph_nSi(GeF_2Cl)_{4-n}$$

(n = 1, 2, 3)

$$\mathrm{2GeF_2 + Ph_2GeCl_2 \longrightarrow Ph_2Ge(GeF_2Cl)_2}$$

$$\begin{tikzcd}
\mathrm{Ph_2Ge(GeF_2Cl)_2} \arrow[r, "\mathrm{MeMgI}"] \arrow[d, "\text{decomposition}"] & \mathrm{Ph_2Ge(GeMe_3)_2} \\
\mathrm{Ph_2GeF_2 + GeF_2 + GeCl_2} &
\end{tikzcd}$$

Chart 1. Some insertion reactions of difluorogermylene.

The study of some organofluorosilanes and -germanes has been the subject of a Ph.D. thesis (16).

The preparation of amine complexes of organodihalogermanium hydrides has been patented (17). The reactions of these with organic halides provide a convenient route to diorganodihalogermanes (18):

$$\begin{tikzcd}
\mathrm{R^1GeX_3 + R_nNH_{3-n} + SiH_4} \arrow[d, "0\text{-}120^\circ\mathrm{C}"] \\
\mathrm{R_nNH_{3-n}H\underset{\substack{|\\ R^1}}{Ge}X_2} \arrow[d, "\mathrm{R^2X}"] \\
\mathrm{R^2GeR^1X_2 + R_nNH_{3-n}HX}
\end{tikzcd}$$

(R,R^1 and R^2 = alkyl, alkenyl, aryl etc.; X = Cl, Br;
n = 0-3)

Fomina et al. accomplished the synthesis of some alkylhalogermanes by γ-irradiation of a mixture of a tetraalkylgermane and a tetrahalogermane (19).

Some new complexes of dichlorogermylene ($:GeCl_2$) have been prepared via the ligand replacement reactions of the type (20):

$$\underset{\text{(dioxane complex)}}{GeCl_2 \cdot C_4H_8O_2} + Ph_3P \xrightarrow[\text{reflux}]{\text{THF}} \underset{\text{(Yield:- 95\%)}}{GeCl_2 \cdot Ph_3P}$$

$$GeCl_2 \cdot C_4H_8O_2 + Ph_3As \longrightarrow \underset{\text{(Yield:- 100\%)}}{GeCl_2 \cdot Ph_3As}$$

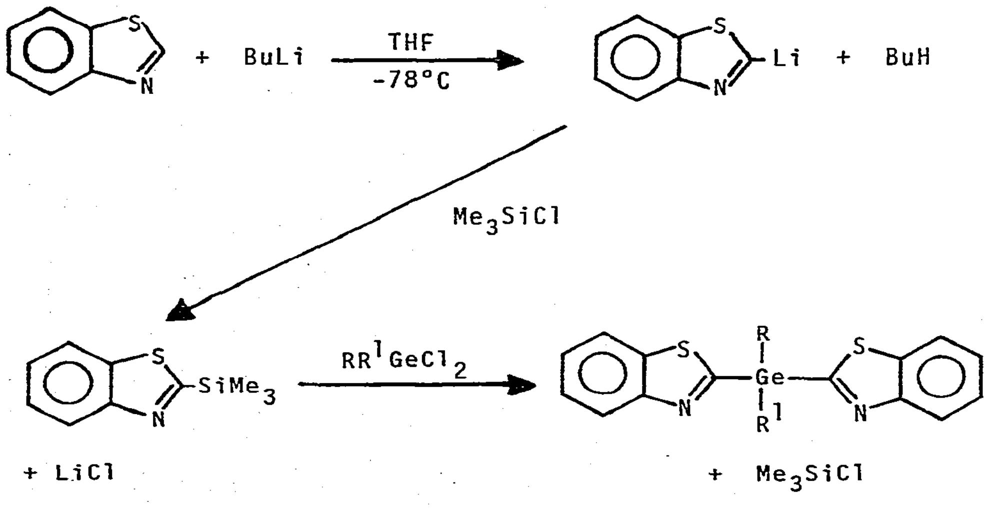
These complexes are convenient sources of monomeric dichlorogermylene.

Reduction (using hypophosphite) of germanium tetrachloride followed by the reaction of the compound with hydrogen iodide has been claimed to be a rapid nonaqueous route to germanium (II) iodide (21):

$$GeCl_4 + NaH_2PO_2 \cdot H_2O \xrightarrow{\text{MeOH}} Ge(HPO_3) + NaCl + 3HCl$$

$$Ge(HPO_3) + 2HI \rightleftharpoons GeI_2 + H_3PO_3$$

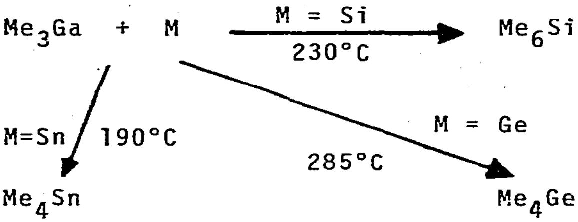
The exchange reactions of benzothiazol-2-yltrimethylsilane with chlorogermanes have been shown to yield di-, tri-, and tetrabenzothiazol-2-ylgermanes (22):



($R = R^1 = Me, Cl$; $R = Me, R^1 = Cl$; $R = R^1 = Cl, C_7H_4NS$; $R = Cl, R^1 = C_7H_4NS$)

Alkylation and arylation

Schlyer and Ring observed the transfer of methyl groups from trimethylgallium to silicon, germanium and tin films (23):



The relative rates of the surface reaction are in the order: Sn > Si > Ge. This order correlates with the electronegativities of the metalloids. The methyl group being readily transferred to the less electronegative tin and silicon and transferred with more difficulty to germanium.

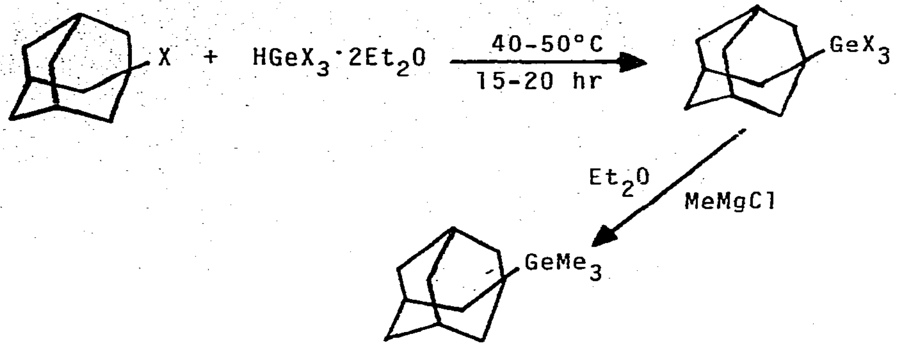
A new synthetic route for the formation of the carbon-germanium bond has been reported (24). It has been shown that Grignard reagents activated by catalytic quantities of nickel (II) complexes can substitute the germanium-hydrogen bond:

$$R^1R^2R^3GeH + RMgX \xrightarrow[Et_2O]{Ni(II)} R^1R^2R^3GeR$$

(R, R^1, R^2, R^3 = alkyl or aryl)

The yields depend on both the catalyst and the Grignard reagent. In every case the stereochemistry of the original organogermane is retained.

The preparation of germyladamantanes has been achieved according to the reaction (25):



(X = Cl, yield:- 75%; X = Br, yield:- 28%)

The reactivity of 1-bromoadamantane has been observed to be considerably more than that of secondary alkyl bromides.

A review on stable homoleptic metal alkyls (including those of germanium) has appeared (26).

Germanium-hydrogen compounds

The preparation of bromogermane and dibromogermane in yields of 50% each has been achieved via the reaction of bromine with germane (27):

$GeH_4 + Br_2 \longrightarrow H_3GeBr + HBr$

$GeH_4 + 2Br_2 \longrightarrow H_2GeBr_2 + 2HBr$

Cradock reported that chlorogermane may be readily prepared from the reaction:

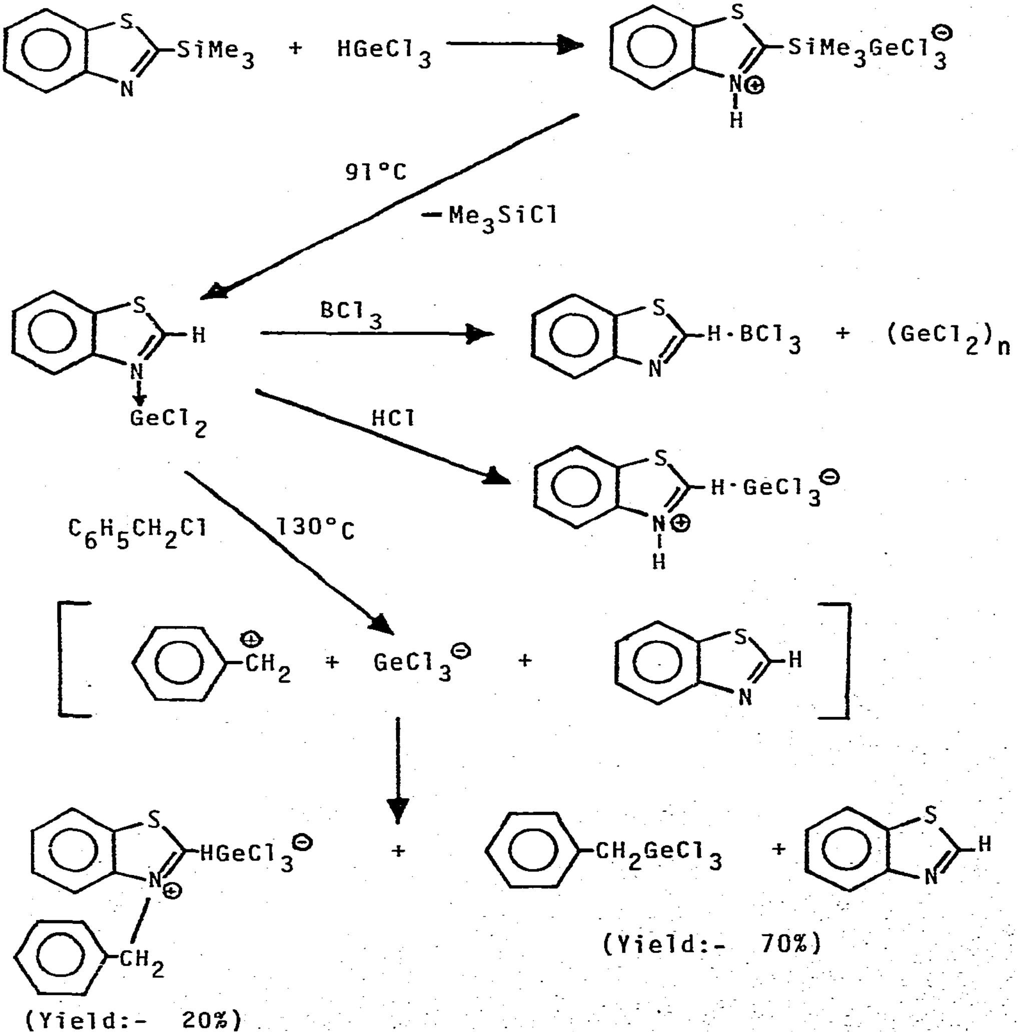
$GeH_4 + SnCl_4 \longrightarrow H_3GeCl + HCl + SnCl_2$

at room temperature (28). The reaction is retarded by the hydrogen chloride produced, and hence it must be removed periodically if complete conversion of germane is required. The reaction of chlorogermane with hydrogen iodide (28) and the fluorination of bromogermane with lead(II)fluoride (29) has been used to synthesize iodogermane and fluorogermane respectively.

$$H_3GeCl + HI \longrightarrow H_3GeI + HCl$$

$$2H_3GeBr + PbF_2 \longrightarrow 2H_3GeF + PbBr_2$$

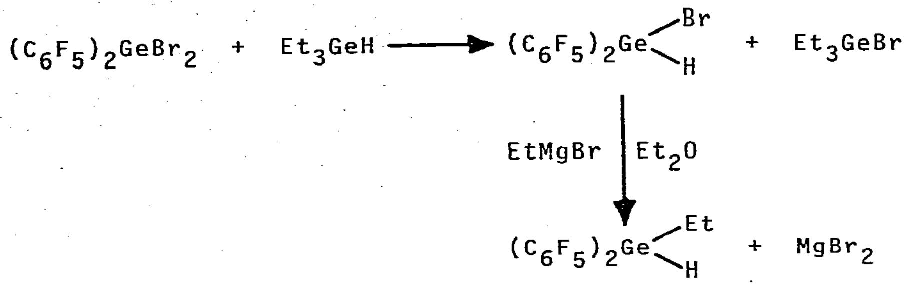
Jutzi and coworkers found that the reaction of benzothiazol-2-yltrimethylsilane with trichlorogermane gave 2-trimethylsilylbenzothiazolium trichlorogermanate, from which the monomeric benzothiazoledichlorogermylene could be obtained (30, 31).



Some pentafluorophenylgermanium hydrides have been synthesized via the following reactions (32):

$$(C_6F_5)_{4-n}GeBr_n \xrightarrow[PhMe\ +\ Et_2O]{LiAlH_4} (C_6F_5)_{4-n}GeH_n$$

(n = 1,2,3)

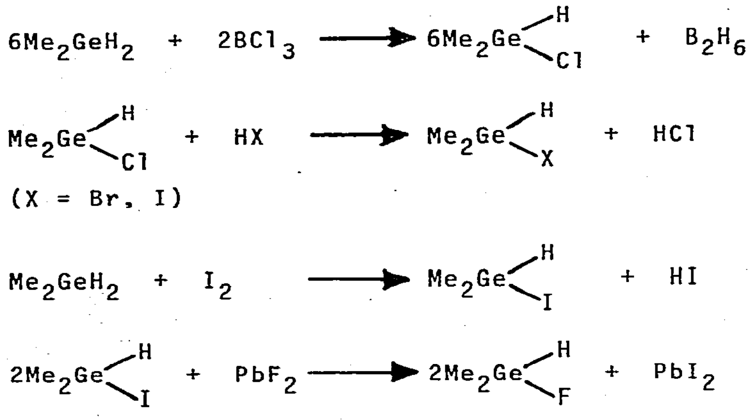


$$(C_6F_5)_2GeBr_2 + Et_3GeH \longrightarrow (C_6F_5)_2Ge(Br)H + Et_3GeBr$$

$$(C_6F_5)_2Ge(Br)H \xrightarrow{EtMgBr,\ Et_2O} (C_6F_5)_2Ge(Et)H + MgBr_2$$

(Yield:- 25%)

The monohalogen derivatives of dimethylgermane have been prepared according to the following reactions (33):



$$6Me_2GeH_2 + 2BCl_3 \longrightarrow 6Me_2Ge(H)Cl + B_2H_6$$

$$Me_2Ge(H)Cl + HX \longrightarrow Me_2Ge(H)X + HCl$$

(X = Br, I)

$$Me_2GeH_2 + I_2 \longrightarrow Me_2Ge(H)I + HI$$

$$2Me_2Ge(H)I + PbF_2 \longrightarrow 2Me_2Ge(H)F + PbI_2$$

Satgé et al. reported the use of some exchange and photochemical reactions to synthesize selectively and quantitatively various substituted phenylgermanes. Some of their results (34) are summarized in Chart 2.

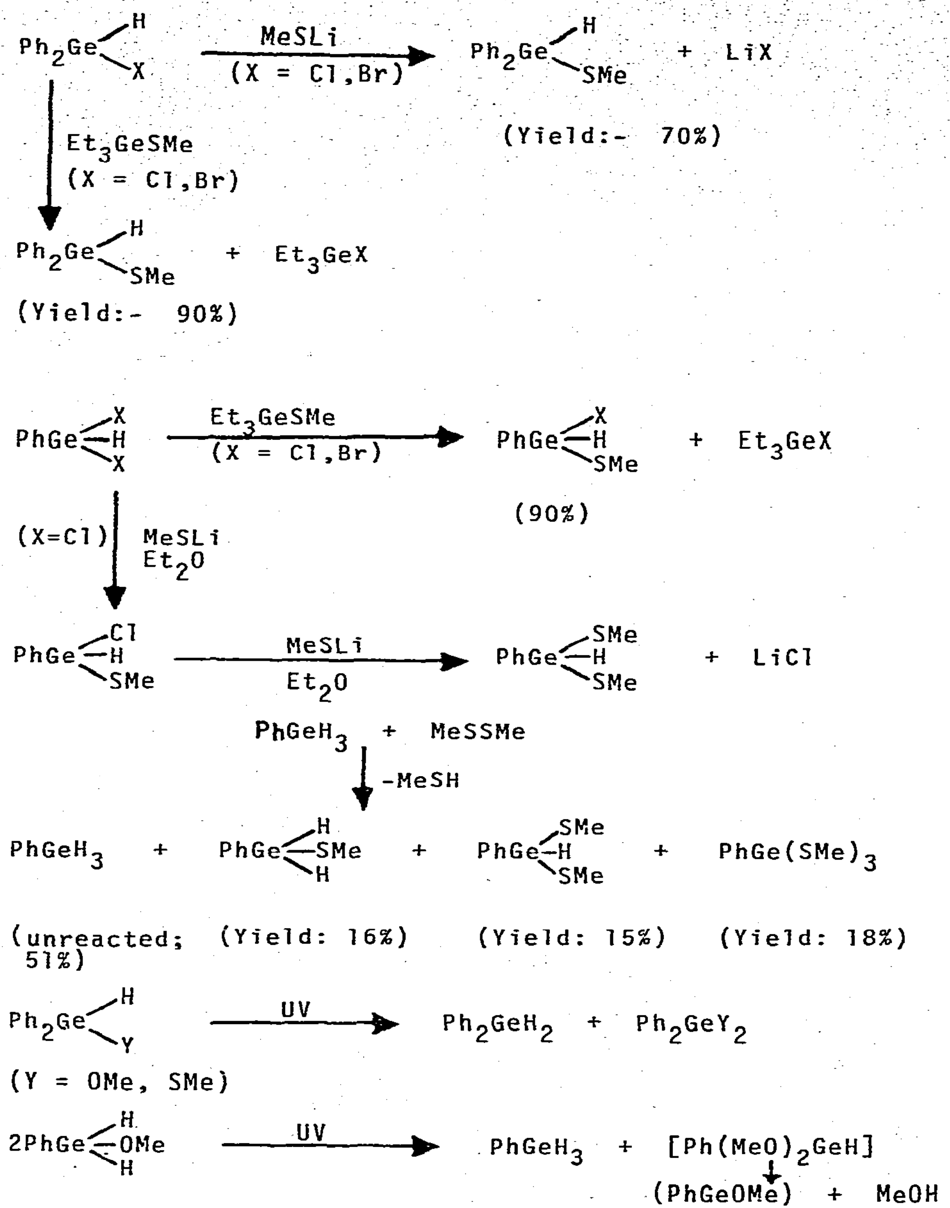
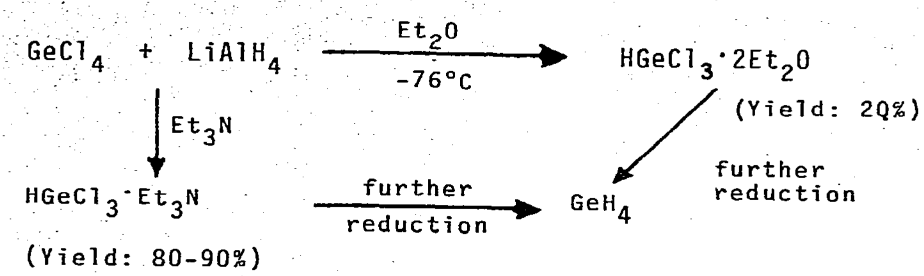


Chart 2. Synthesis of some phenylgermanes

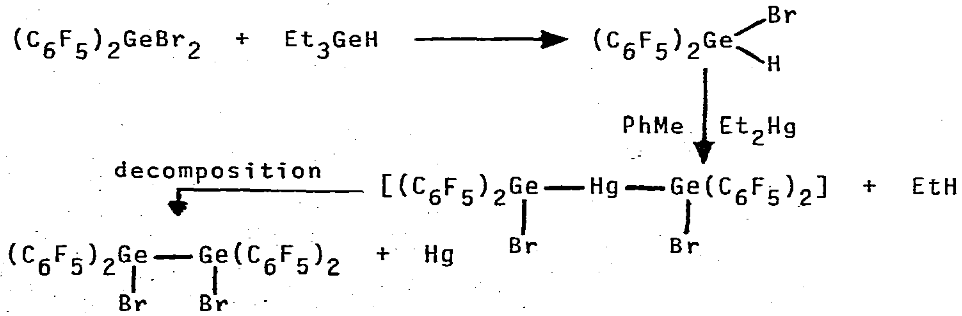
The results of the lithium aluminum hydride reduction of germanium tetrachloride indicate the reaction to be stepwise (35):



The increase in yield of germane at higher temperatures can be explained in terms of the formation of etherate. A still greater yield can be obtained by using solvents that do not complex with germanium tetrachloride. Thus the yield of germane increased to 63% when the reaction was carried out in hexane. According to the authors the yield of germane should depend on the salt-like nature of the complex and should decrease with an increase in the latter. Thus when $HGeCl_3 \cdot 2Et_2O$ and $HGeCl_3 \cdot Et_3N$ were reduced under comparable conditions the yield of germane in the latter case was lower by a factor of five.

Germanium-metal compounds

Vyazankin and coworkers extended their studies on the preparation and reactions of organogermyl-mercury derivatives containing pentafluorophenyl fragments (32,36). These are summarized in Chart 3.

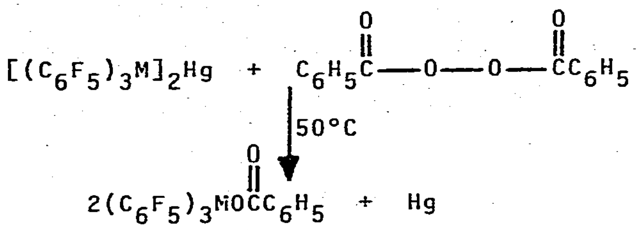


$$(C_6F_5)_2GeBr_2 + Et_3GeH \longrightarrow (C_6F_5)_2GeBrH \xrightarrow[PhMe]{Et_2Hg} [(C_6F_5)_2GeBr{-}Hg{-}GeBr(C_6F_5)_2] + EtH$$

$$[(C_6F_5)_2GeBr{-}Hg{-}GeBr(C_6F_5)_2] \xrightarrow{\text{decomposition}} (C_6F_5)_2GeBr{-}GeBr(C_6F_5)_2 + Hg$$

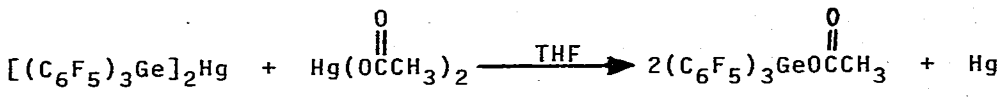
$$Et_3GeHgGe(C_6F_5)_3 + (C_6F_5)_3SnBr \xrightarrow{UV} (C_6F_5)_3GeHgSn(C_6F_5)_3 + Et_3GeBr$$

(Yield:- 31%)



$$[(C_6F_5)_3M]_2Hg + C_6H_5\overset{O}{\overset{\|}{C}}-O-O-\overset{O}{\overset{\|}{C}}C_6H_5 \xrightarrow{50°C} 2(C_6F_5)_3MO\overset{O}{\overset{\|}{C}}C_6H_5 + Hg$$

(M = Ge, Yield:- 41%; M = Sn, Yield:- 74%)

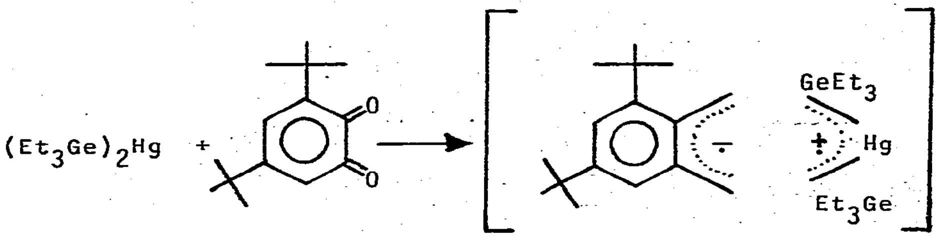


$$[(C_6F_5)_3Ge]_2Hg + Hg(O\overset{O}{\overset{\|}{C}}CH_3)_2 \xrightarrow{THF} 2(C_6F_5)_3GeO\overset{O}{\overset{\|}{C}}CH_3 + Hg$$

(Yield:- 55%)

Chart 3. Synthesis and reactions of some organogermyl-mercury derivatives.

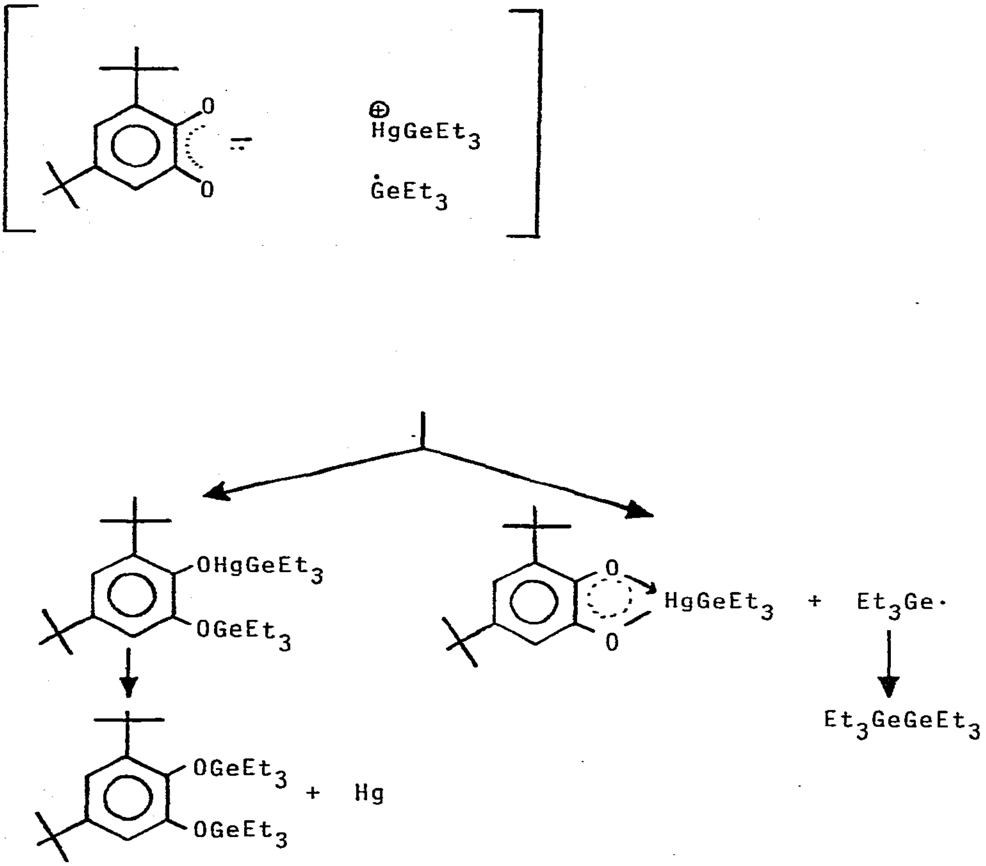
The reaction of bis(triethylgermyl)mercury with 3,5-di-tertiary butyl-1,2-benzoquinone has been investigated (37). It has been shown by means of electron spin resonance spectroscopy that the primary reaction step is a one-electron transfer from a germyl mercurial compound to quinone. Thus the first reaction step is initiated through the generation of the ion-radical pair:



The germylmercury cation radical is not stabilized by its internal charge and electron delocalization and hence it decomposes:

$$(Et_3Ge)_2Hg^{+\cdot} \longrightarrow Et_3Ge^{\cdot} + Et_3GeHg^{+}$$

Further transformation depends on the relative importance of the processes:

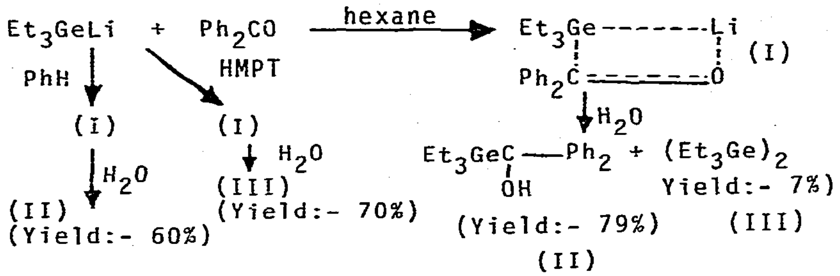


Germylmetallic compounds Et_3GeM^1 (M^1 = Li, Na, K, Rb and Cs) have been prepared in high yield in n-hexane or benzene (38):

$$(R_3M)_2Hg \;+\; 2M^1 \xrightarrow[\text{n-hexane}]{\text{benzene}} 2R_3MM^1 \;+\; Hg$$

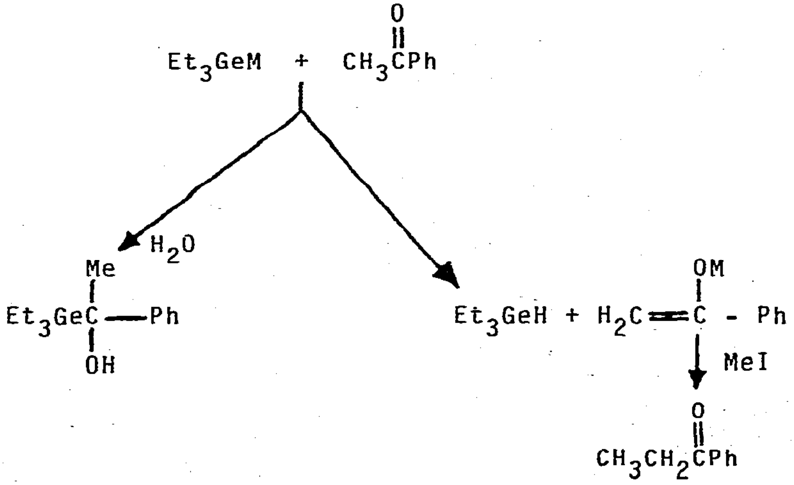
$(R = Et,\ i\text{-}Pr;\ M = Si,\ Ge;\ M^1 = Li,\ Na,\ K,\ Rb,\ Cs)$

The reaction of Et_3GeM^1 with benzophenone, acetophenone and phenylacetylene has been examined. The course of these reactions (i.e. the composition and the yields of the various products) is strongly dependent on the solvating ability of the solvent and the nature of the alkali metal.

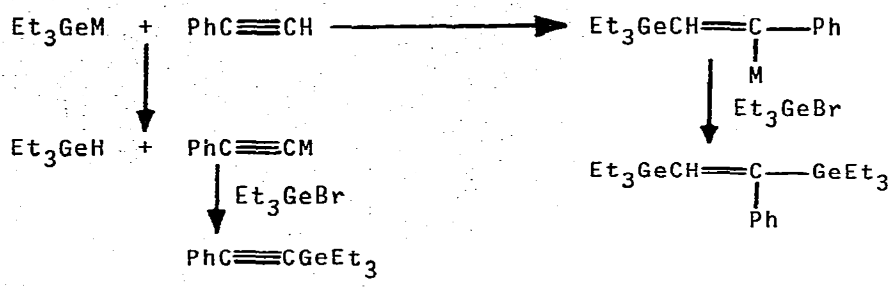


These results could be interpreted in terms of nucleophilic attack of the Et_3Ge^- anion at the carbonyl carbon.

Some other reactions of these germylmetallic derivatives include:

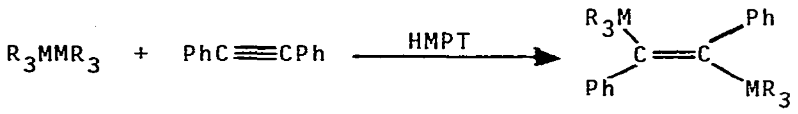


(M = Li, K, Rb)



(M = Li, K)

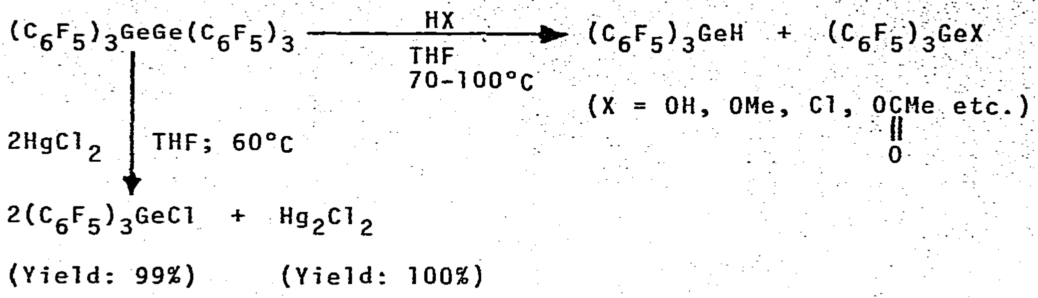
Bulten and Budding investigated the appreciably enhanced reactivity of the metal-metal bond under polar conditions (39). These authors observed the smooth addition of hexaalkyl-ditins and -digermanes to carbon-carbon triple bond systems in HMPT solution and in the presence of a catalytic amount of a base (e.g. MeONa, MeLi, Li) to give exclusively the corresponding trans adducts.



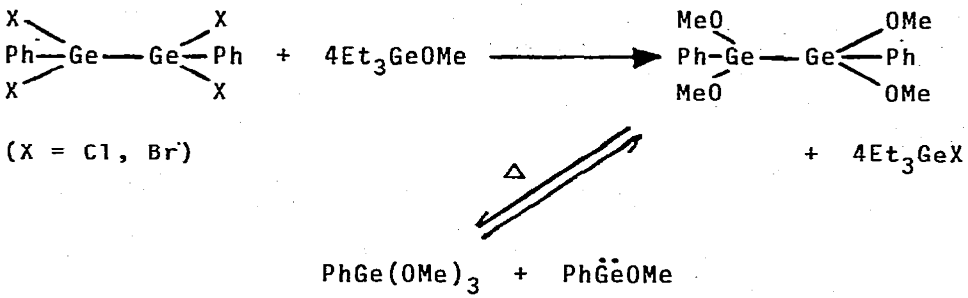
(M = Sn, R = Me, Et; M = Ge, R = Me)

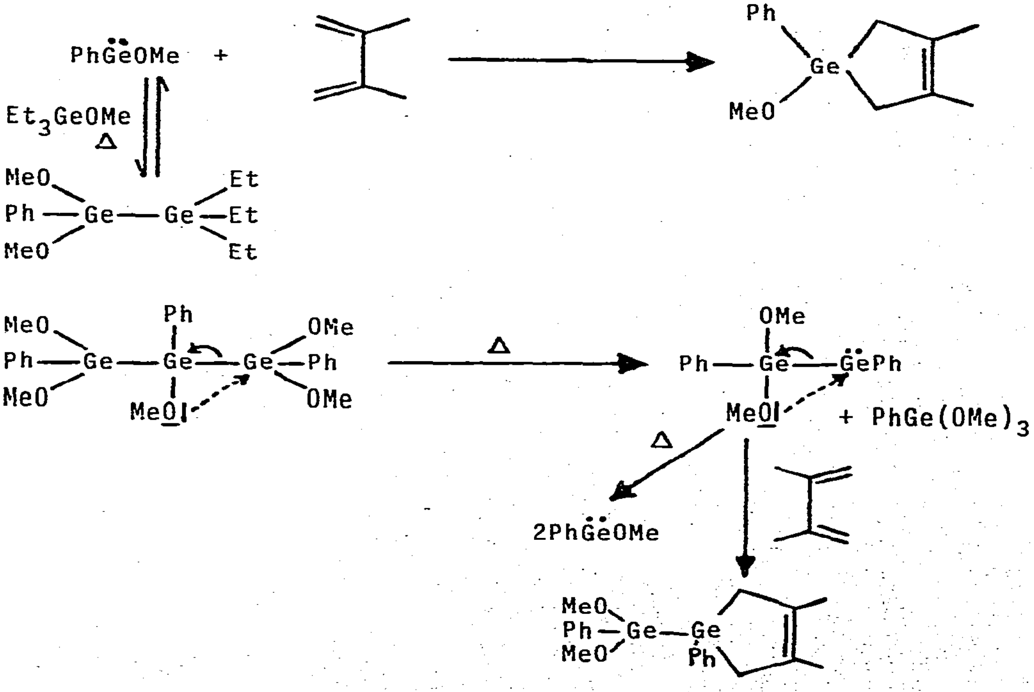
Unlike hexaphenyldigermane, hexakis(pentafluorophenyl)-digermane, has been shown to react with water, methanol, acetic acid etc. via the cleavage of the germanium-germanium bond (40). The reactions proceed in tetrahydrofuran but under identical conditions do not take place in non-polar solvents such as hexane, benzene and toluene etc.

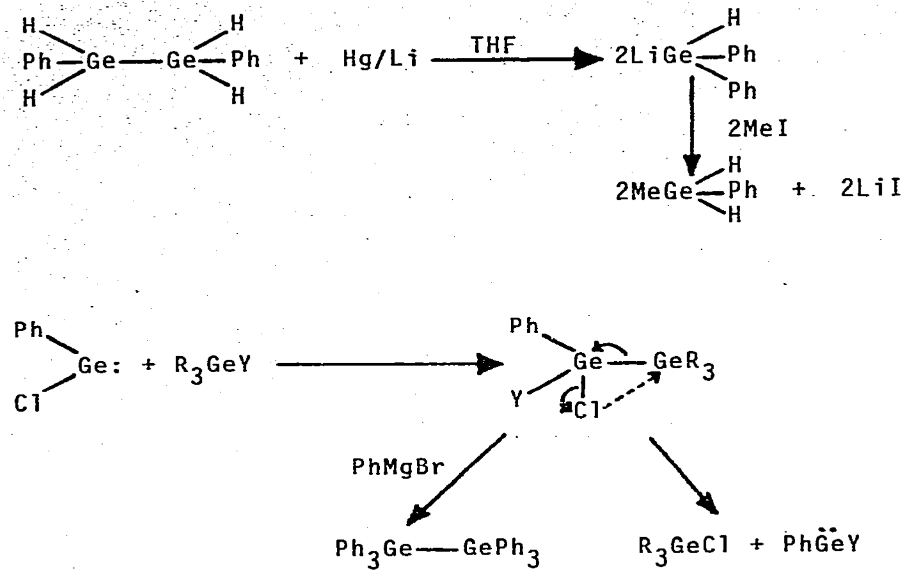
Satgé and coworkers studied the synthesis and thermolysis of polygermanes and observed these reactions to provide



divalent germanium species (34, 41, 42) which could be used for a variety of other syntheses (see Chart 4).







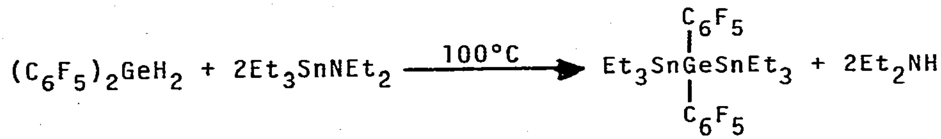
(R = alkyl or phenyl; Y = MeO, MeS, Me_2N, Et_2P)

Chart 4. Reactions of polygermanes.

A synthetic route to some germanium-tin bonded derivatives involves the reaction (32):

$$(C_6F_5)_3GeH + Et_3SnNEt_2 \xrightarrow[100°C]{PhH} (C_6F_5)_3GeSnEt_3 + Et_2NH$$

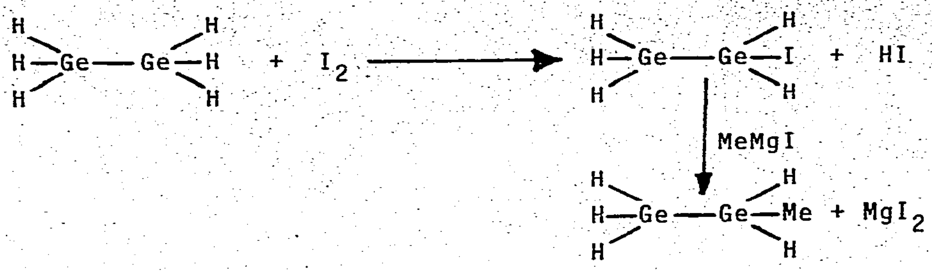
(Yield:- 45%)



$$(C_6F_5)_2GeH_2 + 2Et_3SnNEt_2 \xrightarrow{100°C} Et_3SnGe(C_6F_5)_2SnEt_3 + 2Et_2NH$$

The preparation of some chlorosilylgermanes has been the subject of a Ph.D. thesis (43).

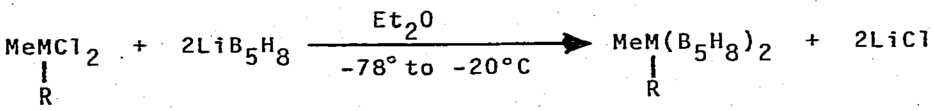
Mackay accomplished the synthesis of iododigermane and methyldigermane according to the scheme (44):



Gaines and Ulman synthesized some boron containing Group IV compounds via the following reactions (45, 46):

$$2\text{-}Me_3GeB_5H_8 + n\text{-}BuLi \xrightarrow[-78^\circ \text{ to } -40^\circ C]{Et_2O;\ 2\ hrs} 2\text{-}Me_3GeB_5H_7^{\ominus}Li^{\oplus}$$

$$\begin{tikzcd}[column sep=small] 2\text{-}Me_3GeB_5H_7^{\ominus}Li^{\oplus} & + \arrow[d] & 1/3\ B_2H_6 & + & 1/3\ BCl_3 \\ Me_3MB_6H_9 & + & LiCl & & \end{tikzcd}$$



$$\underset{\substack{| \\ R}}{MeMCl_2} + 2LiB_5H_8 \xrightarrow[-78^\circ \text{ to } -20^\circ C]{Et_2O} \underset{\substack{| \\ R}}{MeM}(B_5H_8)_2 + 2LiCl$$

(M = Si, R = H, Me; M = Ge, R = Me, Yield:~ 20%)

The reaction of metal carbonyl cation derivatives with a variety of heteroatom borane anions to form 1:1 σ-bonded complexes (47) and the syntheses, characterization and properties of some germacarboranes (48) have been reported. Some of these are listed in Chart 5.

$$\begin{tikzcd}[column sep=small] {[1,2\text{-}GeCHB_{10}H_{10}]^{\ominus}} & + \arrow[d, "(CH_3)_2CO"] & {[(\pi\text{-}C_5H_5)Fe(CO)_2(cyclohexene)]^{\oplus}} \\ (\pi\text{-}C_5H_5)Fe(CO)_2GeCHB_{10}H_{10} & & \end{tikzcd}$$

$$\begin{tikzcd}[column sep=small] {[1,2\text{-}GeCHB_{10}H_{10}]^{\ominus}} & + \arrow[d, "(CH_3)_2CO"] & {[(\pi\text{-}C_7H_7)Mo(CO)_3]^{\oplus}} \\ (\pi\text{-}C_7H_7)Mo(CO)_2GeCHB_{10}H_{10} & & \end{tikzcd}$$

$$\begin{tikzcd}[row sep=large]
{[(\pi\text{-}C_7H_7)Mo(CO)_3]BF_4 \; + \; Cs[GeCHB_{10}H_{10}]} \arrow[d, "\text{2 hrs}"', "(CH_3)_2CO;\ \text{reflux}"] \\
{(\pi\text{-}C_7H_7)Mo(CO)_2GeCHB_{10}H_{10}} \\[-2em]
\text{(Yield:- 33\%)}
\end{tikzcd}$$

$$\begin{tikzcd}[row sep=large]
{Na_3B_{10}H_{10}CH(THF)_2 \; + \; GeCl_4} \arrow[d, "\text{0°C; 3 hrs. followed by addition of MeI}"] \\
{1,2\text{-}B_{10}H_{10}CHGeMe} \\[-2em]
\text{(Yield:- 27\%)} \arrow[d, "\text{piperidine,PhH reflux; 19 hrs}"', "\text{followed by addition of } Me_4N^{\oplus}Cl^{\ominus}"] \\
{Me_4N[B_{10}H_{10}CHGe]} \\[-2em]
\text{(Yield:- 33\%)} \arrow[d, "\text{THF}"', "Cr(CO)_6;\ \text{UV; 18 hrs.}"] \\
{Me_4N[1,2\text{-}B_{10}H_{10}CHGeCr(CO)_5]}
\end{tikzcd}$$

Chart 5. Complexes of some heteroatom boranes.

The reactions of transition metal hexacarbonyls with germanium (II) and tin (II) halides could be used to synthesize the neutral complexes containing metal-metal bond (49):

$$\begin{tikzcd}[row sep=large]
{M(CO)_6 \; + \; CsGeCl_3} \arrow[r, "\text{UV}", "\text{THF}"'] \arrow[d, "SnX_2"', "\text{UV THF}"] & {Cl_2GeM(CO)_5 \; + \; CsCl \; + \; CO} \arrow[d, "Me_4N^{\oplus}Cl^{\ominus}"] \\
{X_2SnM(CO)_5 \; + \; CO} \arrow[d, "Me_4N^{\oplus}X^{\ominus}"] & {[Cl_3GeM(CO)_5]^{\ominus}} \\
{[X_3SnM(CO)_5]^{\ominus}} & \text{(X = Cl, Br, I; M = Cr, Mo, W)}
\end{tikzcd}$$

Some germanium-transition metal bonded derivatives have been prepared according to the following reaction (50):

$$\begin{array}{l} Me_3SiOM'Me_3 \;+\; \pi\text{-}C_5H_5(CO)_3MSiMe_3 \\ \qquad\qquad\Big\downarrow \\ \quad \pi\text{-}C_5H_5(CO)_3MM'Me_3 \;+\; Me_3SiOSiMe_3 \end{array}$$

$(M = Mo, W;\ M' = Ge, Sn)$

Pentacarbonylgermylmanganese could be synthesized via the reaction (51):

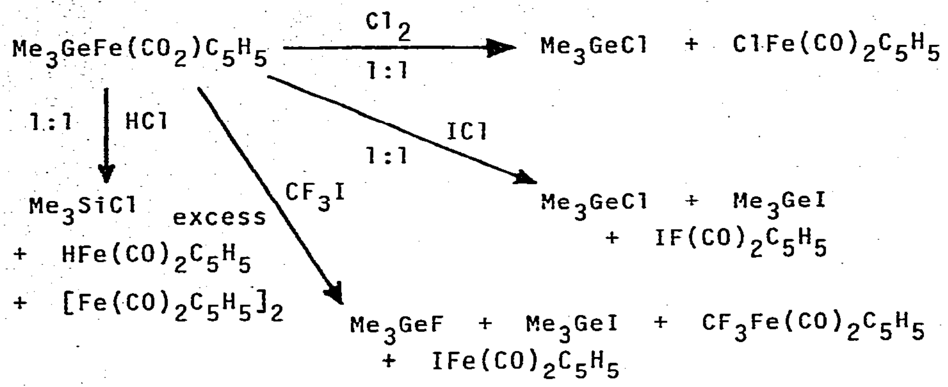
$$H_3GeBr + NaMn(CO)_5 \longrightarrow H_3GeMn(CO)_5 + NaBr$$

Adams observed that the reduction of the dimer, $[(\eta^5\text{-}C_5H_5)Fe(CO)CNCH_3]_2$, with sodium amalgam in tetrahydrofuran leads to the formation of the hydride which engages in a base-catalyzed reaction with Group IV metal halides (52):

$$\begin{array}{l} [(\eta^5\text{-}C_5H_5)Fe(CO)CNMe]_2 \;+\; Na/Hg \\ \qquad\qquad \text{THF}\ \Big\downarrow\ -15°C \\ [(\eta^5\text{-}C_5H_5)Fe(CO)CNMeH] \\ \qquad\qquad -78°C\ \Big\downarrow\ \text{RCl, THF} \\ \quad \eta^5\text{-}C_5H_5Fe(CO)CNMeR \end{array}$$

$(R = CH_2CN,\ Me_2GeCl,\ Me_3Sn)$

The reactions of halogens, halo-acids, etc. (53) and of pentafluorophenyllithium (54) with some trimethyl, triphenyl or phenyl (pentafluorophenyl) Group IV metal-transition metal derivatives have been described. Some of these reactions are summarized in Chart 6.



$$\mathrm{Ph_nGeCl_{4-n} + NaM' \xrightarrow{THF} Ph_nGeCl_{3-n}M' + NaCl}$$

[n = 1 or 2; M' = $\mathrm{Mn(CO)_5}$, $\mathrm{Fe(CO)_2C_5H_5}$]

$$\begin{array}{c}\mathrm{Ph_{3-n}X_nMM' + nC_6F_5Li}\\ \big\downarrow \text{ether}\\ \mathrm{Ph_{3-n}(C_6F_5)_nMM' + nLiX}\end{array}$$

[X = Cl or Br; n = 1-3; M = Si or Ge where M' = $\mathrm{Mn(CO)_5}$ and M = Sn for $\mathrm{Fe(CO)_2C_5H_5}$; and n = 3 for M = Si or Ge where M' = $\mathrm{Fe(CO)_2C_5H_5}$]

Chart 6. Synthesis and reactions of germanium-transition metal bonded derivatives.

The reactivities of the compounds $\mathrm{Ph_{3-n}Cl_nMM'}$ [n = 1-3; M = Si, Ge, Sn; M' = $\mathrm{Mn(CO)_5}$, $\mathrm{Fe(CO)_2C_5H_5}$] toward pentafluorophenyllithium have been found to depend upon M,M' and the number of phenyl groups bonded to the Group IV metal. With M' = $\mathrm{Mn(CO)_5}$ the reactivity decreased in the order:

$Sn \approx Ge > Si$. For $M' = Fe(CO)_2(C_5H_5)$, reaction occurred for all the tin containing species, but for M = Ge or Si only the trichloro derivatives underwent reaction.

Nesmeyanov et al. accomplished the synthesis and studied the reactions of some complexes containing germanium-cobalt

$$4R_nMX_{4-n} + 3Co_2(CO)_8 \longrightarrow 4R_nX_{3-n}MCo(CO)_4 + 2CoX_2 + 8CO$$

$$2R_nMX_{4-n} + 3Co_2(CO)_8 \longrightarrow 2R_nX_{2-n}M[Co(CO)_4]_2 + 2CoX_2 + 8CO$$

$$4R_nMX_{4-n} + 9Co_2(CO)_8 \longrightarrow 4R_nX_{1-n}M[Co(CO)_4]_3 + 6CoX_2 + 24CO$$

(R = Me, Ph; X = Cl, Br, $O\overset{O}{\overset{\|}{C}}CH_3$; M = Ge, Sn; n = 0-3)

$$\begin{tikzcd} R_{4-n}M[Co(CO)_4]_n + EPh_3 \arrow[d, "\text{reflux}"', "\text{heptane}"] \\ R_{4-n}M[Co(CO)_3EPh_3]_n \end{tikzcd}$$

<u>or</u>

$$R_{4-n}M[Co(CO)_4]_m[Co(CO)_3EPh_3]_{n-m}$$

(R = Ph, Cl; M = Ge, Sn; E = P, As, Sb; n = 1, 2)

$$Ph_3Ge[Co(CO)_3PPh_3] + HBr \xrightarrow[CH_2Cl_2]{20^\circ C} PhBr_2Ge[Co(CO)_3PPh_3]$$

(Yield:- 58%)

$$\begin{tikzcd} Cl_2Ge[Co(CO)_3PPh_3][Co(CO)_4] + 2KCNS \arrow[d, "1\ \text{hr.}"', "20^\circ C"] \\ (CNS)_2Ge[Co(CO)_3PPh_3][Co(CO)_4] \end{tikzcd}$$

(Yield:- 70%)

Chart 7. Synthesis and reactions of some germanium-cobalt bonded complexes.

and tin-cobalt bonds (55, 56). Some of their results are compiled in Chart 7.

Some Group IV metal containing nitroso transition metal complexes have been prepared via the following insertion reaction (57):

$$C_5H_5CoNOI \quad + \quad MI_2 \longrightarrow C_5H_5Co(NO)MI_3$$

(M = Ge, Sn)

These new complexes do not associate via nitroso bridges.

The reaction of octacarbonyldicobalt with Group IV metal hydrides gave Group IV metal-cobalt bonded complexes in high yields (58):

$$2R_3MH \quad + \quad Co_2(CO)_8 \longrightarrow 2R_3MCo(CO)_4 \quad + \quad H_2$$

(Yield:- 60-94%)

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

Reaction was judged to be somewhat slower for M = Ge or Sn. Some metal exchange reactions were also studied:

$$\begin{tikzcd}
Me_3SiCo(CO)_4 + Me_3GeH \arrow[r, "PhH", "20^\circ C"'] \arrow[d, "Me_3GeBr", "Et_2O;\ 20^\circ C"'] & Me_3GeCo(CO)_4 + Me_3SiH \\
Me_3GeCo(CO)_4 + Me_3SiBr &
\end{tikzcd}$$

$$\begin{tikzcd}
Me_3GeCo(CO)_4 \arrow[r, "Me_3SnH", "20^\circ C;\ PhH"'] \arrow[d, "Et_2O;\ 20^\circ C", "Me_3SnCl"'] \arrow[dr, "HCl"] \arrow[ddr, "HgCl_2"'] & Me_3SnCo(CO)_4 + Me_3GeH \\
Me_3SnCo(CO)_4 + Me_3GeCl & Me_3GeCl + HCo(CO)_4 \\
 & [Co(CO)_4]_2Hg + Me_3GeCl
\end{tikzcd}$$

Alkynes [C_2Ph_2, MeC_2Ph, PhC_2H and $C_2(COOEt)_2$] have been shown to displace the bridging $GePh_2$ grouping from $[(OC)_3\overline{Co(\mu\text{-}GePh_2)(\mu\text{-}CO)Co}(CO)_3]$ to form the complexes $[(OC)_3\overline{Co(\mu\text{-}alkyne)Co}(CO)_3]$ together with $(Ph_2Ge)_n$ (where n = 4-7). The kinetics of reaction of complex with diphenylacetylene in decalin have been studied over a range of temperaturesand a mechanism has been proposed (59).

Marks and Seyam reported their studies involving halide abstraction reactions of halo-Group IV metal-transition metal compounds and related attempts to generate cationic silylene, germylene and stannylene complexes (60). Some of their results are summarized in Chart 8.

$$(\eta^5\text{-}C_5H_5)Mo(CO)_3Ge(Ph_2)Cl + AgBF_4 \xrightarrow{(CH_3)_2CO} (\eta^5\text{-}C_5H_5)Mo(CO)_3Ge(Ph_2)F + AgCl + BF_3$$

(Yield:- 80%)

$$(OC)_4CoGeCl_3 + AgBF_4 \longrightarrow (OC)_4CoGeF_3 + AgCl + BF_3$$

(Yield:- 60%)

$$(C_5H_5)Mo(CO)_3Ge(Ph_2)Cl + AgSbF_6 \xrightarrow{CH_2Cl_2} (C_5H_5)Mo(CO)_3Ge(Ph_2)F + AgCl + SbF_5$$

$$(C_5H_5)Mo(CO)_3Ge(Ph_2)F + PF_5 \xrightarrow{PhH}$$

$(C_5H_5)Mo(CO)_3Ge(Ph)F_2$

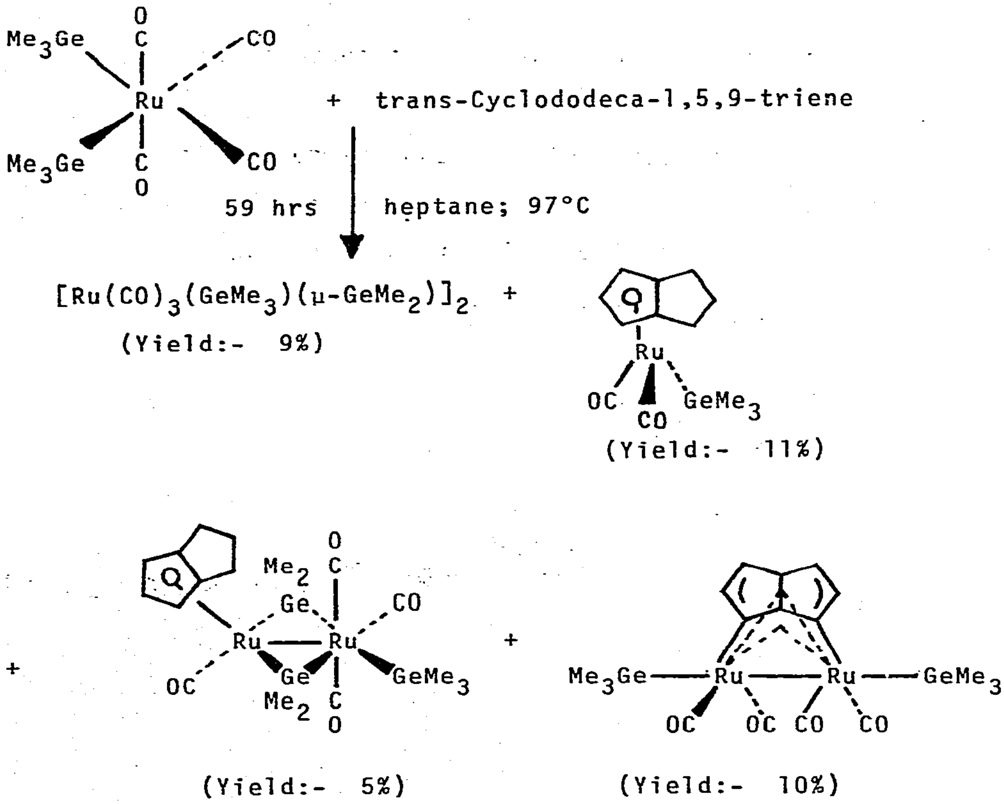
$$\Big\downarrow \text{4.5 days} \quad PF_5$$

$(C_5H_5)Mo(CO)_3GeF_3$

(Yield:- 80%)

Chart 8. Synthesis of some fluorogermyl-transition metal complexes.

The preparation and reactions of a variety of organogermanium-ruthenium complexes have been reported (61-64). These are listed in Chart 9.



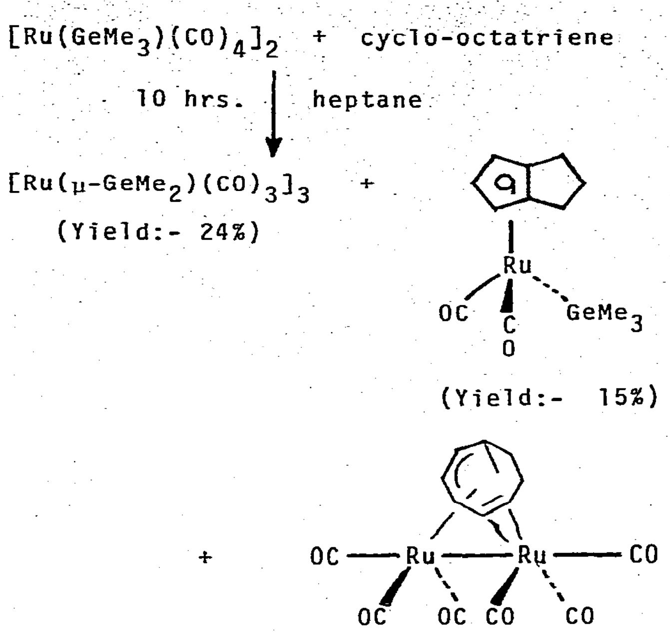
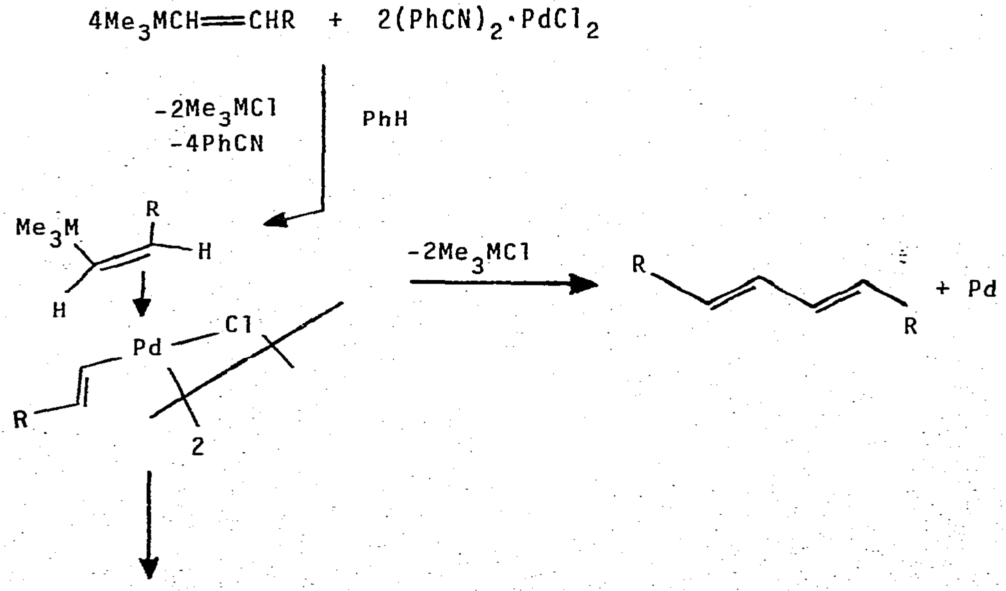


Chart 9. Reactions of organogermyl-ruthenium complexes.

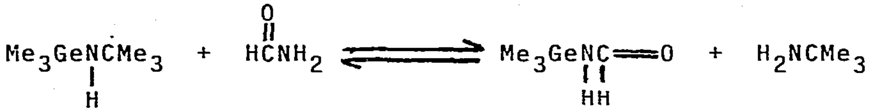
The reactions of vinyl-silanes and -germanes with dichlorobis(benzonitrile)palladium (II) have been reported to proceed according to the following scheme (65):



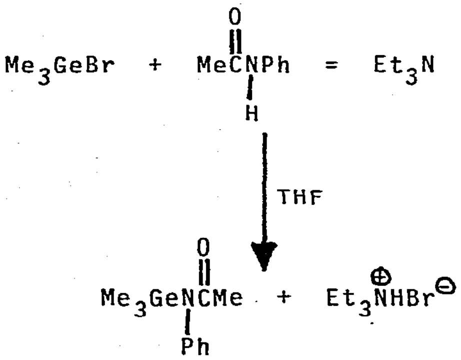
[M = Si, Ge; R = Me or Ph when M = Si]

Germanium-nitrogen compounds

Yoder et al. synthesized a series of trimethylgermyl amides and established the amide structures by IR and NMR measurements (66):



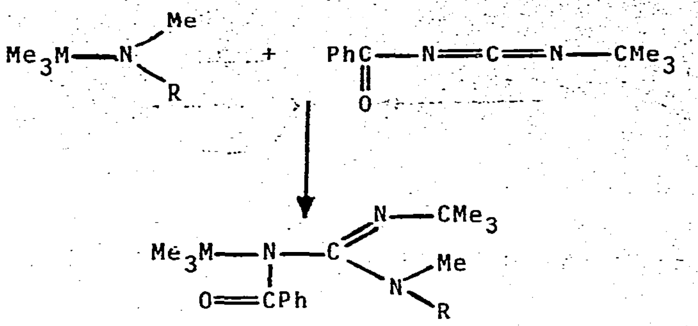
$$Me_3Ge\underset{H}{N}CMe_3 + H\overset{O}{\overset{\|}{C}}NH_2 \rightleftharpoons Me_3Ge\underset{H}{N}\underset{H}{C}{=}O + H_2NCMe_3$$



$$Me_3GeBr + Me\overset{O}{\overset{\|}{C}}\underset{H}{N}Ph = Et_3N \xrightarrow{THF} Me_3Ge\underset{Ph}{N}\overset{O}{\overset{\|}{C}}Me + Et_3\overset{\oplus}{N}HBr^{\ominus}$$

The barrier to rotation and isomer ratios were determined and discussed in relation to those for the carbon and silicon homologs.

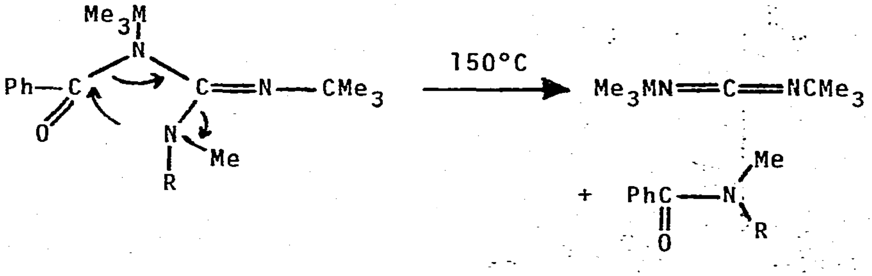
The insertion reaction of benzoyl-tertiary-butyl-carbodiimide with some Group IV metal-nitrogen bonded derivatives have been studied (67).



(Yield:- 63-96%)

[M = Si, R = Me, Me_3Si
M = Ge, R = Me
M = Sn, R = Me, Me_3Sn]

The thermal decomposition of the adducts occurs at 150°C.



(M = Si, Ge; R = Me)

Lappert and Harris reported the preparation and characterization of unusual stable, monomeric, diamagnetic colored, volatile, hydrocarbon-soluble, dialkylamides of the Group IV elements (68).

$$GeCl_2\cdot dioxan + 2LiN(SiMe_3)(CMe_3)\cdot Et_2O$$

$$\Big\downarrow \; 0°C \quad Et_2O$$

$$Ge[N(SiMe_3)(CMe_3)]_2 + 2LiCl$$

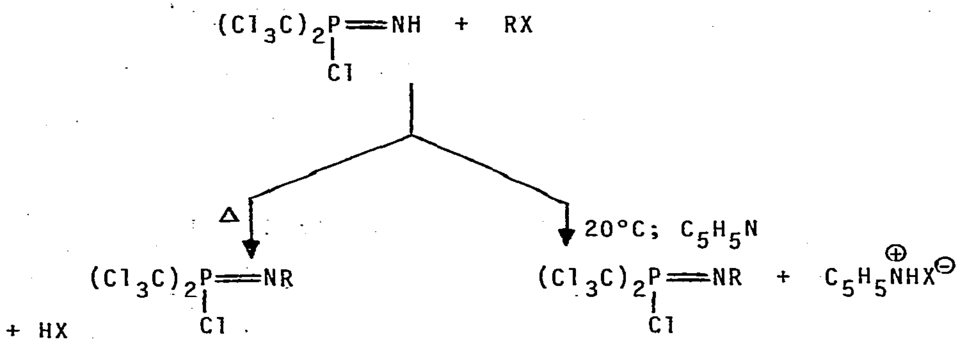
(Yield:- 76%)

$$MCl_2 + 2LiN(SiMe_3)_2Et_2O \xrightarrow[0°C]{Et_2O} M[N(SiMe_3)_2]_2 + 2LiCl$$

(M = Ge, Sn, Pb)

Compounds are thermochromic becoming redder on heating; redness increases in the series Ge <Sn <Pb.

The preparation of some bis(trichloromethyl)chlorophosphazo-silanes and -germanes has been accomplished according to the following reaction (69):



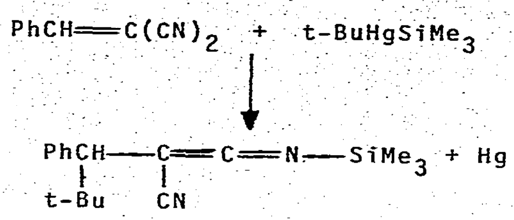
$$(Cl_3C)_2P(Cl){=}NH + RX$$

$$\xrightarrow{\Delta} (Cl_3C)_2P(Cl){=}NR + HX$$

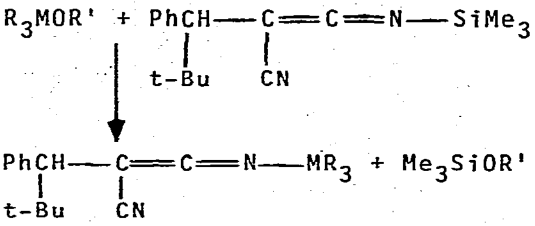
$$\xrightarrow{20°C;\ C_5H_5N} (Cl_3C)_2P(Cl){=}NR + C_5H_5\overset{\oplus}{N}HX^{\ominus}$$

($R = SiCl_3$, $GeCl_3$, X = Cl; $R = SiBr_3$, $GeBr_3$, X = Br;
$R = Me_2SiCl$, X = Cl; $R = Me_3Ge$, X = Br; Yield:- 68-98%)

Mitchell studied the reaction of tertiary-butyl(trimethylsilyl)mercury with benzylidenemalonodinitrile and reported the formation of N-trimethylsilylketeneimine (70):



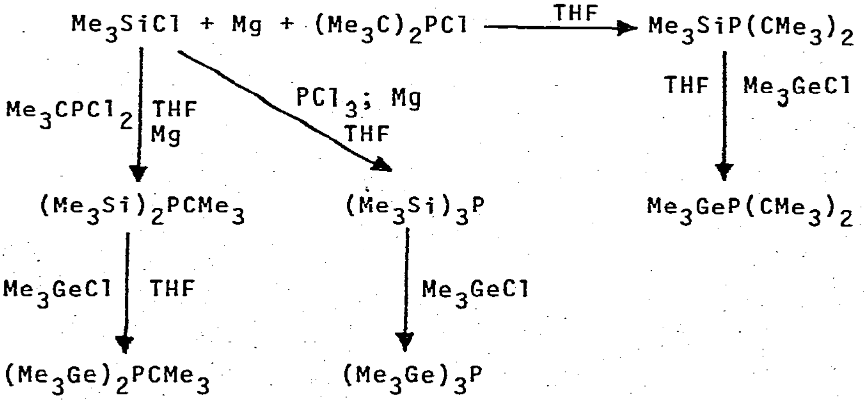
Transmetallation from N-silylketeneimine allows the preparation of N-germyl- or N-plumbylketeneimines.



(M = Ge, Sn, Pb; R = alkyl; R' = Me, COMe)

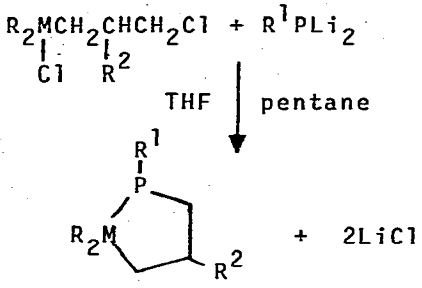
Germanium-phosphorus, -arsenic and -antimony compounds

The exchange reactions of some organosilylphosphines have been utilized to synthesize organogermylphosphines (71):



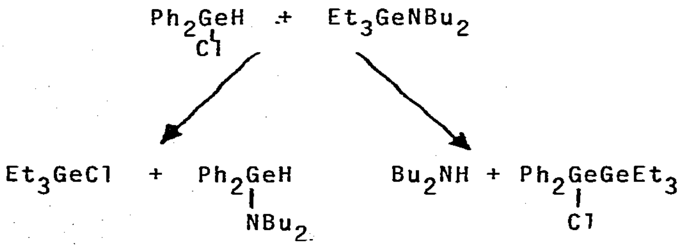
The preparation of some cyclic germanium-phosphorus bonded compounds has been accomplished via the reaction of organochlorogermanes with the dilithio derivatives of secondary phosphines (72):

$$R^1PH_2 + 2\text{-}BuLi \xrightarrow{THF} R^1PLi_2 + 2BuH$$



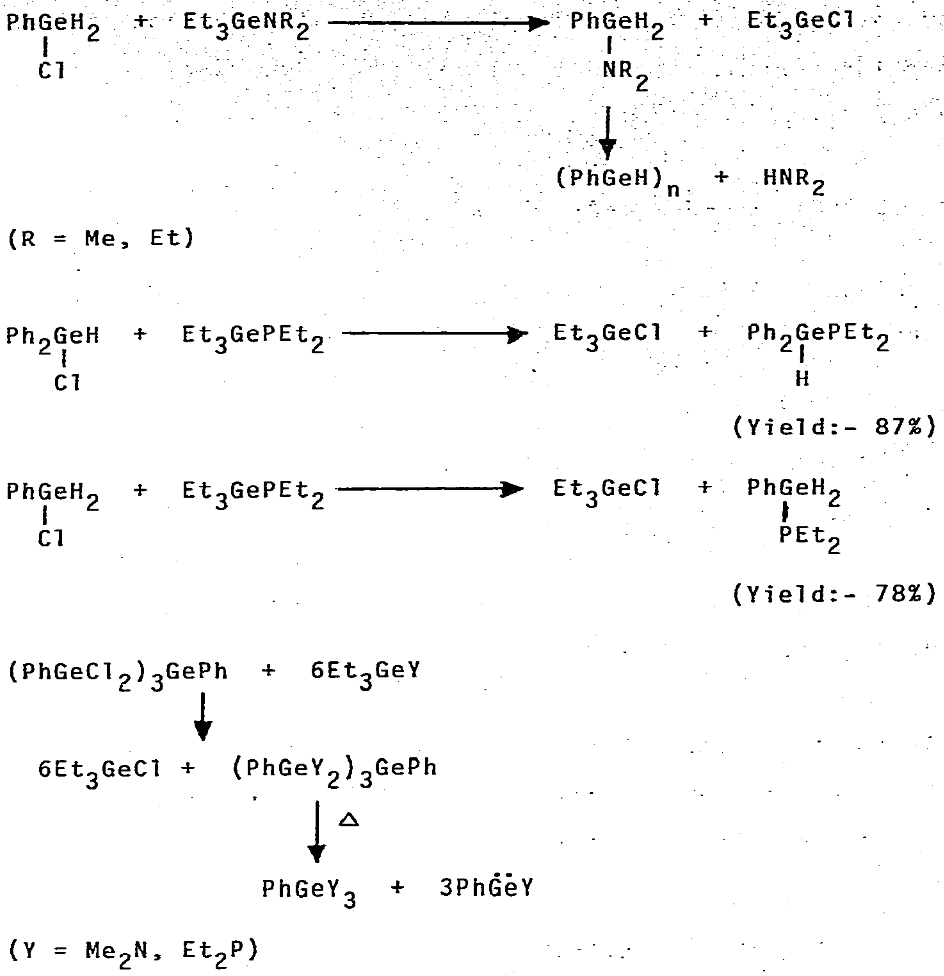
$(M = Si, Ge, Sn; R^1 = Bu, Ph; R_2 = Me_2, Et_2, PhMe;$
$R^2 = H, Me;$ yield:- 60-80%)

Satgé et al. studied the reactions of some organogermyl-amines and -phosphines (41, 42, 73). Some of their results are compiled in Chart 10.



(Yield:- 68%) (Yield:- 32%)

(exchange reaction) (Ge-N bond cleavage)



(R = Me, Et)

(Yield:- 87%)

(Yield:- 78%)

(Y = Me_2N, Et_2P)

Chart 10. Some exchange reactions of organogermyl-amines and -phosphines.

Germylphosphine has been prepared via the following reaction scheme (74):

$$LiAlH_4 + 4PH_3 \xrightarrow{\text{diglyme}} Li[Al(PH_2)_4] + 4H_2$$

$$4H_3GeBr + Li[Al(PH_2)_4] \xrightarrow{\text{diglyme}} 4H_3GePH_2 + LiBr + AlBr_3$$

The subject of organophosphorus-metal bonded compounds has appeared as a book chapter (75).

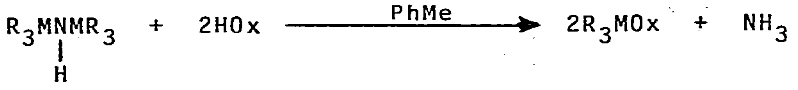
Organometal-stibine substituted complexes of nickel could be synthesized according to the reaction (76):

$$(Me_3M)_3Sb + Ni(CO)_4 \longrightarrow (Me_3M)_3Sb\text{-}Ni(CO)_3 + CO$$

(M = C, Si, Ge, Sn)

Germanium-oxygen compounds

Several tri- and di-organo(oxinato)-silanes and -germanes have been synthesized (77):



$$R_3M\underset{H}{\underset{|}{N}}MR_3 + 2HOx \xrightarrow{PhMe} 2R_3MOx + NH_3$$

$$\left[R_2M\underset{H}{\underset{|}{N}}\right]_n + 2HOx \longrightarrow R_2M(Ox)_2 + NH_3$$

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

The UV-spectra indicate that the compounds involve either chelated or non-chelated oxinato groups or both depending on the number and kind of organic groups on the metal atom. Thus both trimethyl(oxinato)germane and dimethyl(dioxinato)-germane, are non-chelated, with a coordination number of four and diphenyldi(oxinato)germane, is chelated, with a coordination number of six.

Mehrotra and coworkers continued their studies on the preparative routes (see Chart 11) to dibutylgermanium dioximates (78) and reviewed the chemistry of O-organometal hydroxylamines and oximes (79).

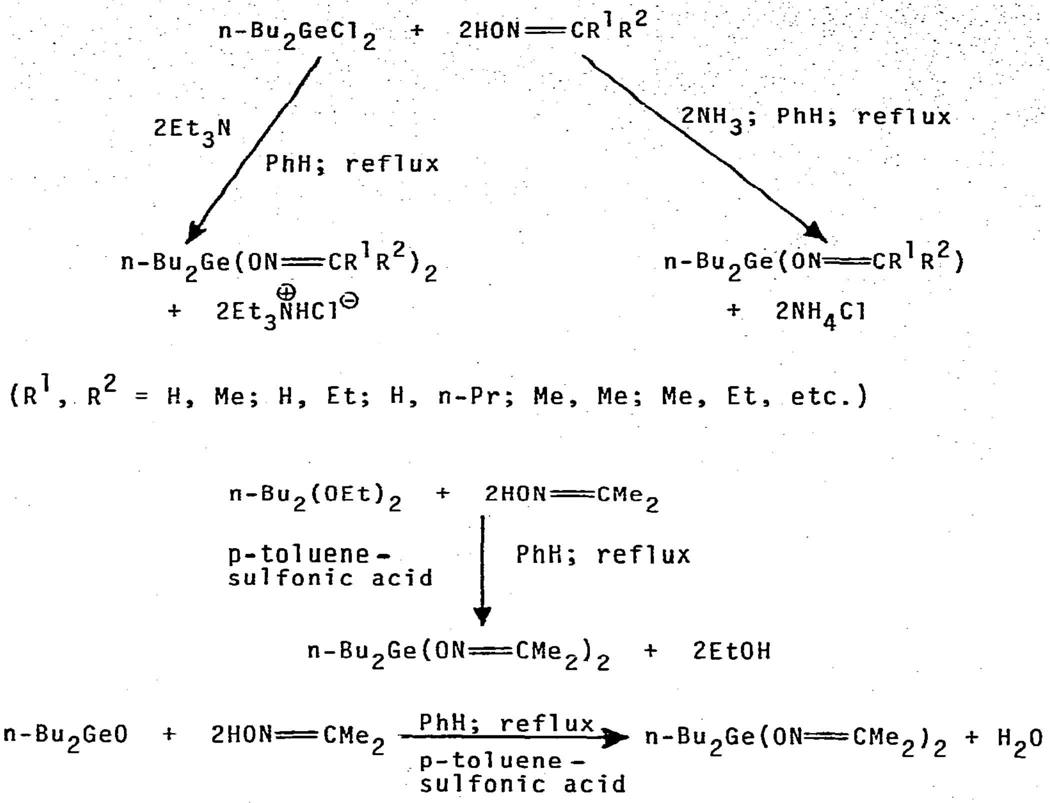
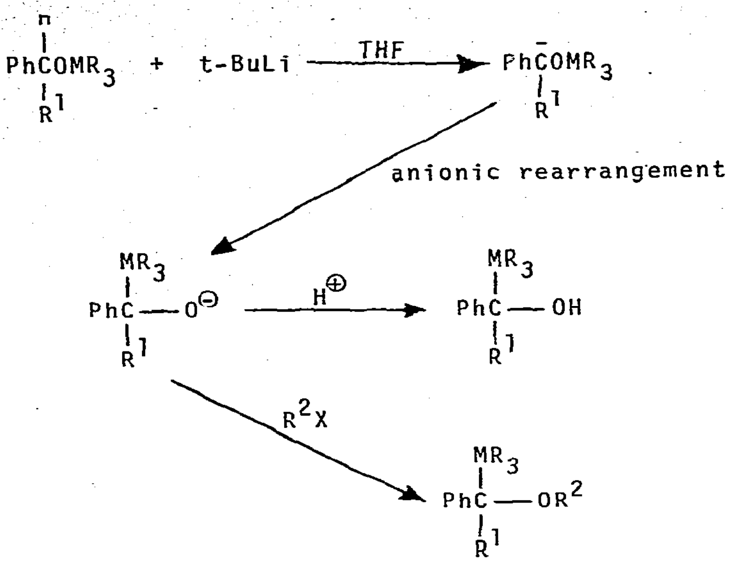


Chart 11. Preparation of some n-dibutylgermanium dioximates.

It has been shown that benzyloxyorgano-silanes and -germanes, upon metallation at the benzyl carbon atom with excess tertiary butyllithium or lithium diisopropylamide in tetrahydrofuran, rearrange rapidly via a 1,2-shift of silicon or germanium to the α-carbanion to give, in high yield, anions of α-hydroxy-α-trimethylmetal toluene. These anions can be protonated or alkylated at oxygen (80).

Various conditions and solvent systems are discussed in order to achieve the metallation rapidly and selectively at the benzylic position.

The synthesis of hexalkylgermastannoxanes could be



accomplished by heating a mixture of bis(trialkyltin)oxide and bis(trialkylgermanium)oxide (81):

$$(Me_3Ge)_2O \quad + \quad (Bu_3Sn)_2O \longrightarrow Me_3GeOSnBu_3$$

Insertion reactions of phenyl isocyanate and chloral into $\gt Ge{-}O{-}Ge\lt$ and $\gt Ge{-}O{-}Sn\lt$ bonds are reported.

The acetoxy derivatives of silicon, germanium and tin have been shown to be less active toward phogene than the alkoxy derivatives, and the reactivity declined in the order: $Sn > Ge > Si$ (82).

Lindner and Schardt reported the synthesis of a number of sulfinic acid derivatives of Group IV elements by the reaction of anhydrous aliphatic and aromatic silver sulfinates, RSO_2Ag, with organo-Group IV element halides (83-85):

$$R_3GeBr \quad + \quad AgO_2SR^1 \xrightarrow[20^\circ C]{THF} R_3GeO_2SR^1 \quad + \quad AgBr$$

($R = R^1 = Et$; $R = Me$, $R^1 = Ph$; $R = Ph$, $R^1 = p\text{-}MeC_6H_4$, Me, Et)

$$\mathrm{R_2GeCl_2 + 2AgO_2SR^1 \xrightarrow[20^\circ C]{THF} R_2Ge(O_2SR^1)_2 + 2AgCl}$$

$(\mathrm{R = Ph,\ R^1 = Me,\ Ph,\ p\text{-}MeC_6H_4;\ R = Me,\ R^1 = Me,\ Ph,\ p\text{-}MeC_6H_4})$

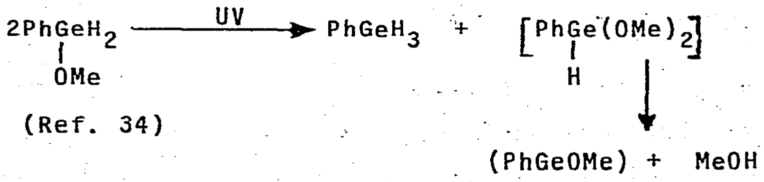
$$\mathrm{MeGeCl_3 + 3AgO_2SMe \xrightarrow[20^\circ C]{THF} MeGe(O_2SMe)_3 + 3AgCl}$$

The ester-like structure and the trigonal pyramidal configuration of the R_3M group results unequivocally from various spectroscopic investigations.

The preparation and reactions of a variety of germanium-oxygen bonded derivatives have been reported (32,34,41,42,86,87).

$$\mathrm{(C_6F_5)_{4-n}GeBr_n + nEt_3SnOMe \xrightarrow[reflux]{PhH} (C_6F_5)_{4-n}Ge(OMe)_n + nEt_3SnBr}$$

(Ref. 32)



$$\begin{tikzcd} \mathrm{2PhGeH_2(OMe)} \arrow[r, "UV"] & \mathrm{PhGeH_3} + \mathrm{[PhGeH(OMe)_2]} \arrow[d] \\ & \mathrm{(PhGeOMe) + MeOH} \end{tikzcd}$$

(Ref. 34)

$$\begin{tikzcd} \mathrm{Ph_3GeOH + Et_2Zn} \arrow[r, "PhMe", "90^\circ C"'] & \mathrm{Ph_3GeOZnEt} \arrow[d, "Me_3COOH"] \\ & \mathrm{Ph_3GeOZnOOCMe_3} \end{tikzcd}$$

(Ref. 86)

$$\mathrm{[(RO)_2P]_2O + R^1{}_3MOR^2 \longrightarrow (RO)_2POMR^1{}_3}$$

$(\mathrm{R,\ R^1,\ = alkyl\ or\ aryl;\ R^2 = alkyl;\ M = Group\ IV\ metal})$

(Ref. 87)

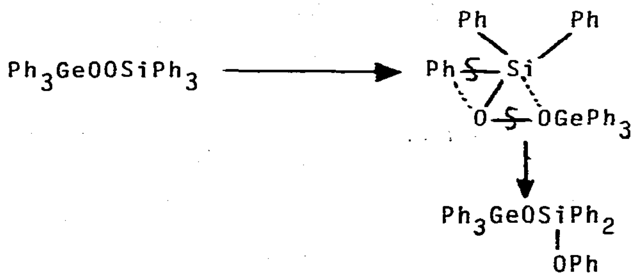
A review article on organo-siloxy, -germoxy and -stannoxy derivatives of boron has appeared (88).

Yablokov and coworkers reported the synthesis of peroxides containing the $\geq\mathrm{GeOOSi}\leq$ fragment by the reaction of triphenylgermylhydroperoxide with organochlorosilanes in the presence of ammonia (89):

$$Ph_3GeOOH \; + \; R_3SiCl \xrightarrow[\text{dry } NH_3]{Et_2O} Ph_3GeOOSiR_3 \; + \; NH_4Cl$$

(R = Me, Et, i-Pr, n-Bu, Ph etc.)

Within the range of 90-170°C the peroxides rearrange into isomeric, non-peroxide compounds in quantitative yield.



The exchange reaction between tris(trimethylsilylmethyl)stannyllithium and organogermanium peroxide has been reported to proceed as (90):

$$\begin{tikzcd}(Me_3SiCH_2)_3SnLi \; + \; Ph_3GeOOCMe_3 \arrow[d, "THF"', "20^\circ C"] \\ (Me_3SiCH_2)_3SnOOCMe_3 \; + \; Ph_3GeOH\end{tikzcd}$$

(Yield:- 78%)

A review article on organometallic peroxides including those of germanium has appeared (91).

Germanium-sulfur and -selenium compounds

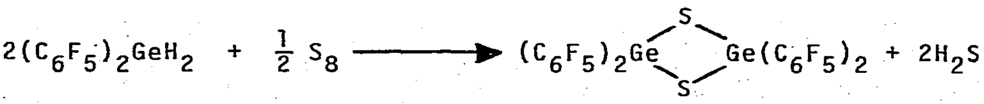
A number of new routes to pentafluorophenyl derivatives with germanium-chalcogen bonds have been reported (40, 92):

$$\begin{tikzcd}
(C_6F_5)_3GeH + \frac{1}{8} S_8 \arrow[r, "135-150^\circ C", "4\ hr."'] & (C_6F_5)_3GeSH \arrow[d, "Et_2Hg", "20-50^\circ C\ 30\ min."'] \\
& (C_6F_5)_3GeSHgEt + EtH
\end{tikzcd}$$

(Yield:- 61%)

$$\begin{tikzcd}
(C_6F_5)_3GeBr + (Et_3Ge)_2X \arrow[d, "150^\circ C"] \\
(C_6F_5)_3GeXGeEt_3 + Et_3GeBr \arrow[d, "(C_6F_5)_3GeBr"] \\
[(C_6F_5)_3Ge]_2X + Et_3GeBr
\end{tikzcd}$$

(X = S, Se)

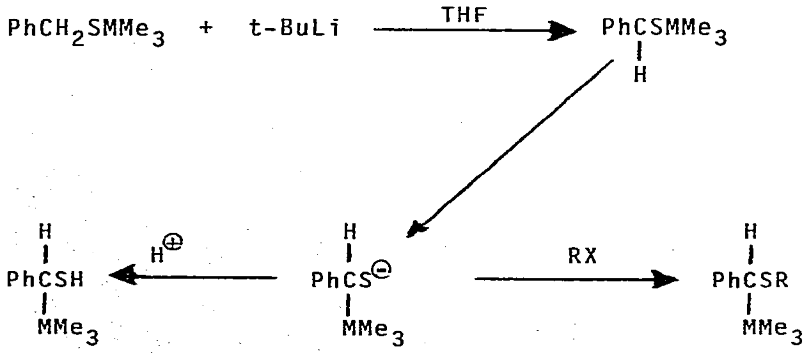


$$4(C_6F_5)GeH_3 + \frac{3}{2} S_8 \longrightarrow (C_6F_5)_4Ge_4S_6 + 6H_2S$$

Analogous reaction of phenyltrichlorogermane with hydrogen sulfide in pyridine-benzene mixture gave corresponding phenyl derivative, $Ph_4Ge_4S_6$, of adamantane structure in 25% yield (93). It is interesting to note that in compounds of the type, $(C_6F_5)_3GeXGeEt_3$ (where X = S, Se), the $-XGeEt_3$ bond is more reactive than the $-XGe(C_6F_5)_3$ bond as indicated by exchange reactions of the type:

$$(C_6F_5)_3GeXGeEt_3 + (C_6F_5)_3SnBr \longrightarrow (C_6F_5)_3GeXSn(C_6F_5)_3 + Et_3GeBr$$

Wright and West observed that benzylthiotrimethylsilane and -germane [analogous to corresponding oxy derivatives (80)] upon metallation at the benzyl carbon atom with excess tertiary butyllithium or lithium diisopropylamide in tetrahydrofuran, rearrange rapidly via 1,2-shift of silicon or germanium to the α-carbanion to give, in high yield, anions of α-mercapto-α-trimethylmetaltoluene (94):

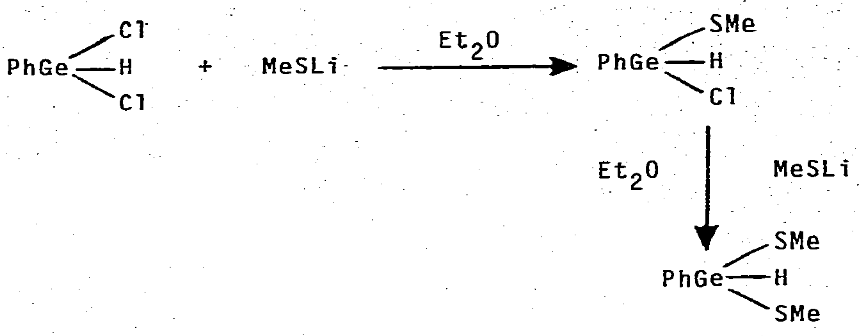


$$\begin{tikzcd}[column sep=small] & PhCH_2SMMe_3 + t\text{-}BuLi \arrow[r, "THF"] & \underset{\displaystyle H}{PhC}SMMe_3 \arrow[dl] \\ \overset{\displaystyle H}{\underset{\displaystyle MMe_3}{PhC}}SH & \overset{\displaystyle H}{\underset{\displaystyle MMe_3}{PhC}}S^{\ominus} \arrow[l, "H^{\oplus}"'] \arrow[r, "RX"] & \overset{\displaystyle H}{\underset{\displaystyle MMe_3}{PhC}}SR \end{tikzcd}$$

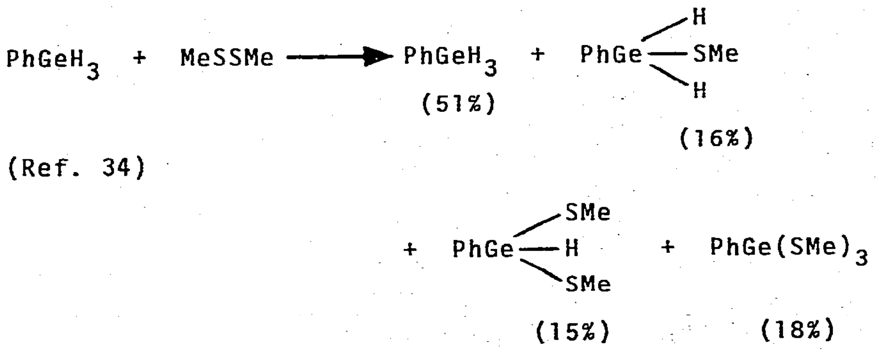
(M = Si, Ge)

Optimum conditions are discussed to achieve the desired anion.

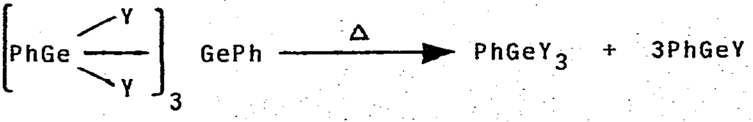
The preparation of a number of germanium-sulfur bonded compounds has been accomplished according to the reactions (34, 41, 42, 95):



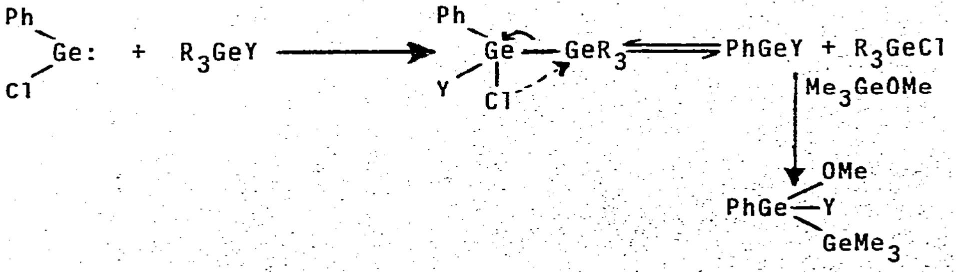
(Ref. 34)



(Ref. 34)



(Ref. 41) (Y = MeS-, Me_2N-, Et_2P-)



(Ref. 42) (Y = MeO-, MeS-, Me_2N-)

$$2H_3GeBr + Li_2S \longrightarrow (H_3Ge)_2S + 2LiBr$$

(Ref. 95)

The preparation and studies of mixed silyl and germyl chalcogens via the reactions of the type:

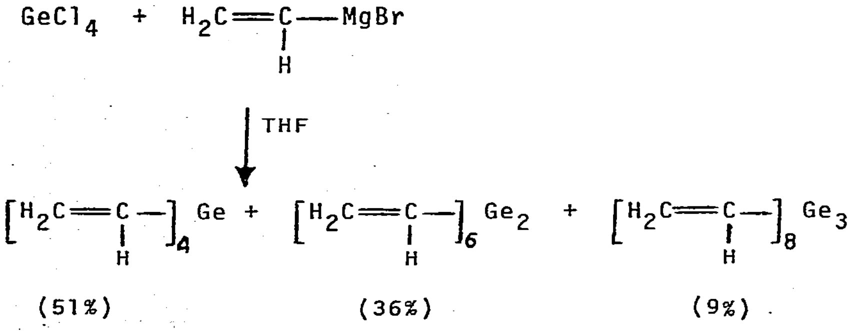
$$H_3GeCl + (H_3Si)_2S \longrightarrow H_3GeSSiH_3 + H_3SiCl$$

$$H_3GeF + (Me_3Si)_2S \longrightarrow H_3GeSSiMe_3 + Me_3SiF$$

have been the subject of a Ph.D. thesis (96).

Alkenyl- and alkynyl-germanium compounds

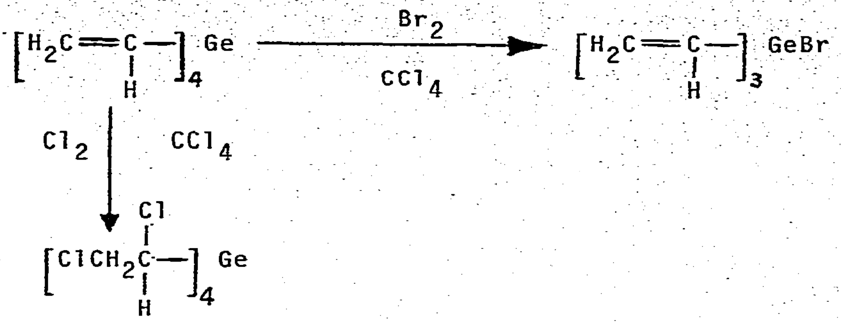
Glockling et al. observed that the reaction of Group IV metal tetrachlorides, MCl_4 (where M = Si, Ge or Sn) with vinylmagnesium bromide yields tetravinyl derivatives as the major product for M = Si or Sn, but in the case of germanium two products are formed in comparable yield (97):



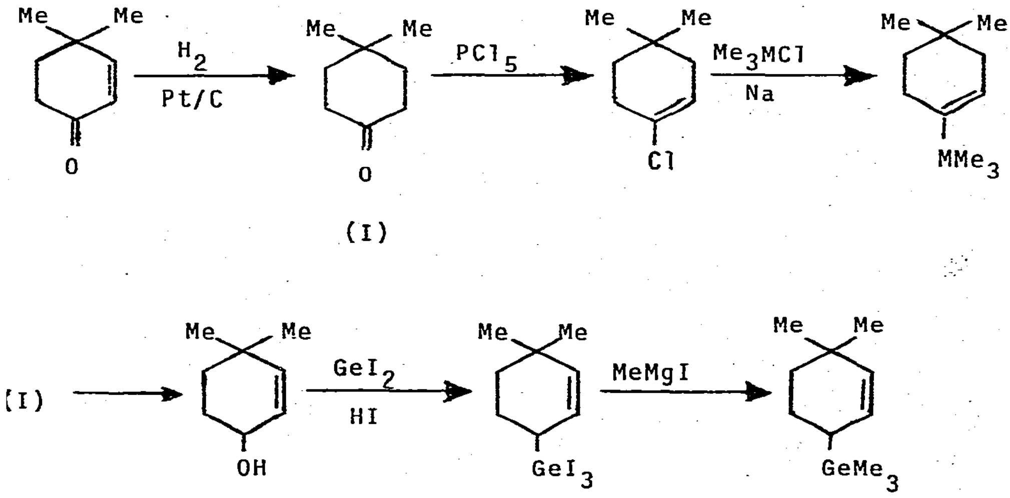
$$GeCl_4 + H_2C{=}\underset{\substack{|\\H}}{C}{-}MgBr \xrightarrow{THF} \Big[H_2C{=}\underset{\substack{|\\H}}{C}{-}\Big]_4Ge + \Big[H_2C{=}\underset{\substack{|\\H}}{C}{-}\Big]_6Ge_2 + \Big[H_2C{=}\underset{\substack{|\\H}}{C}{-}\Big]_8Ge_3$$

(51%) (36%) (9%).

Some reactions of tetravinylgermane are reported:



The preparation of some trimethyl-silyl- and -germyl-cyclohexene derivatives has been reported (98):

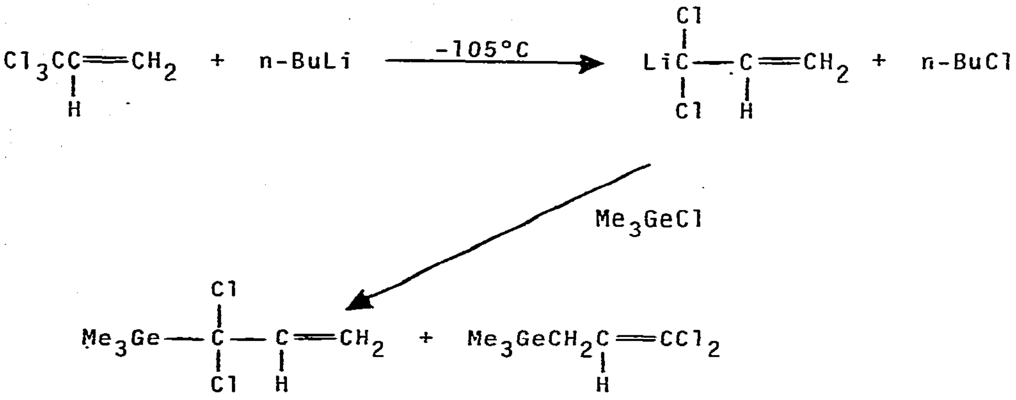


The stereochemistry of the hydroboration of these alkenes is reported.

The chlorovinyl compounds of germanium could be prepared via the reaction (99):

$$n\text{-}Bu_3GeH + (ClCH{=}CH)_2Hg \xrightarrow{Et_2O} n\text{-}Bu_3Ge(CH{=}CHCl) + Hg + H_2$$

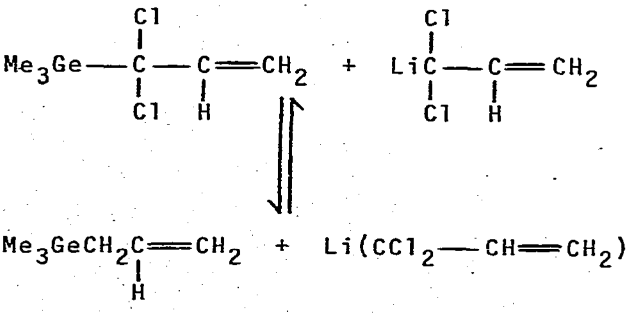
Seyferth and coworkers reported the reaction of gem dichloroallyllithium with a number of halides and observed the reaction with trimethylchlorogermane to proceed as follows (100):



$$Cl_3CCH{=}CH_2 + n\text{-}BuLi \xrightarrow{-105°C} LiCCl_2{-}CH{=}CH_2 + n\text{-}BuCl$$

$$LiCCl_2{-}CH{=}CH_2 \xrightarrow{Me_3GeCl} Me_3Ge{-}CCl_2{-}CH{=}CH_2 + Me_3GeCH_2CH{=}CCl_2$$

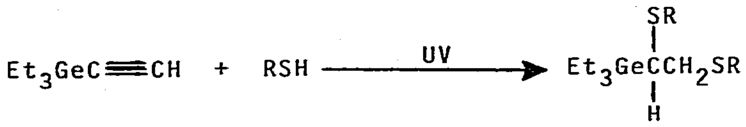
Proton NMR spectroscopy served well in distinguishing these isomers. The other isomer probably arises due to transmetallation equilibria (100):



$$Me_3Ge{-}CCl_2{-}CH{=}CH_2 + LiCCl_2{-}CH{=}CH_2 \rightleftharpoons Me_3GeCH_2CH{=}CH_2 + Li(CCl_2{-}CH{=}CH_2)$$

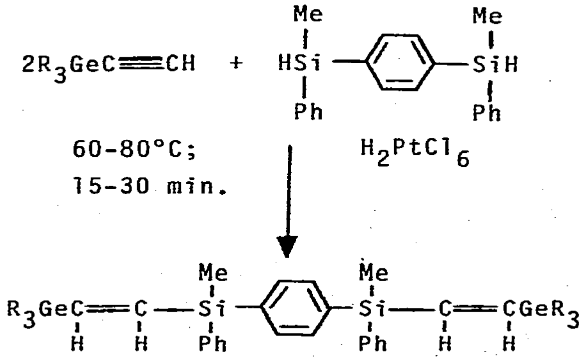
Some publications on topics such as polymerization and copolymerization of 1-triethylgermyl-1,3-butadiene with styrene (101); synthesis of some alkenyl-germanium compounds (102) and the deposition of polymer films on aluminum sheets by exposure of Me_3MR (where R = $-CH{=}CH_2$, $C{\equiv}CH$; M = C, Si, Ge, Sn) type compounds to a glow discharge (103) have appeared.

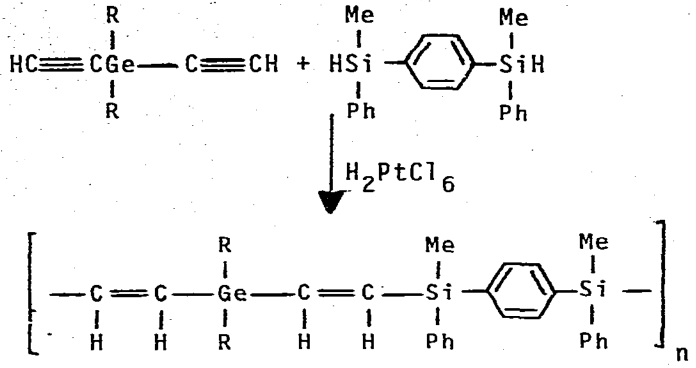
The photochemical reactions of heteroorganic derivatives of acetylene of the type $Et_3MC{\equiv}CH$ (where M = Ge or Sn) with alkanethiols indicated that when M = Ge, even with a deficiency of the thiol only the product of the addition of two molecules of the latter was obtained (104):



$$Et_3GeC{\equiv}CH + RSH \xrightarrow{UV} Et_3Ge\overset{SR}{\underset{H}{C}}CH_2SR$$

Gverdtsiteli and coworkers reported the addition reactions of some germylethylnyl compounds (105, 106):

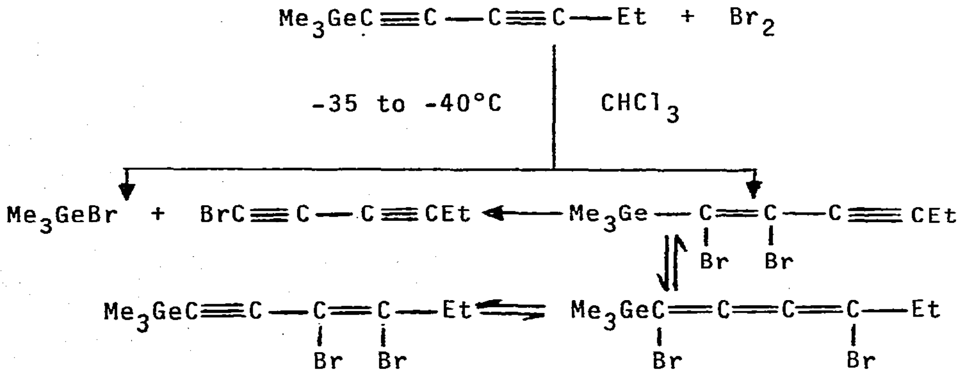




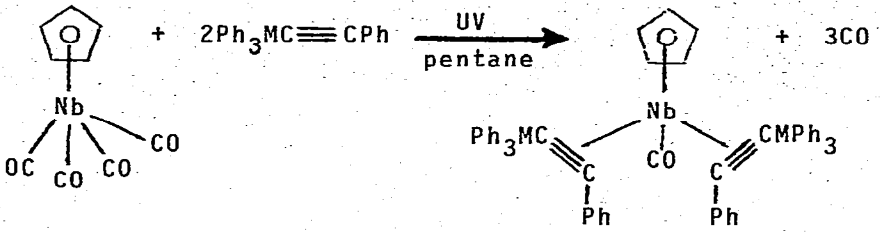
(R = Et, Bu, Ph)

Some electrical properties of the substances synthesized have been studied.

The increase in the polarities of the metal-carbon bonds in the molecules of germanium and tin containing diacetylenic hydrocarbons (most probably as a result of a marked reduction in d_π-p_π interaction) leads to the reduction in stability of this bond toward polar reagents; unlike silicon containing diacetylenic hydrocarbons to which bromine and thiols add at the triple bonds in accordance with their polarization, their germanium and tin containing analogs are split at the metal-carbon bond by these reagents under the same conditions (107).

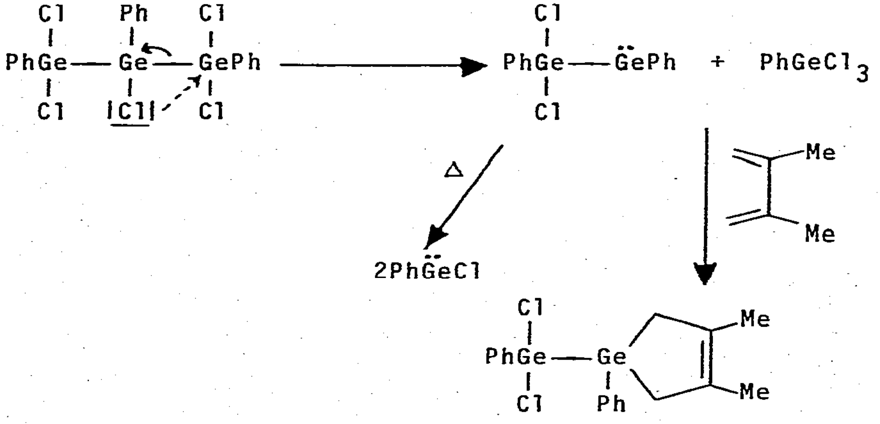


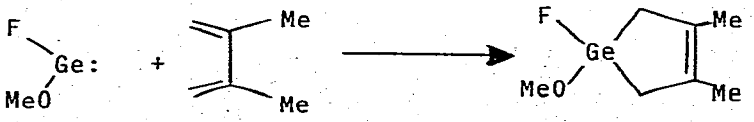
The reaction of some Group IV metal acetylenes with cyclopentadienylniobium tetracarbonyl has been shown to replace three carbonyl groups by two π-acetylenic ligands, independent of the ratio of the reactants (108):



Germacyclanes

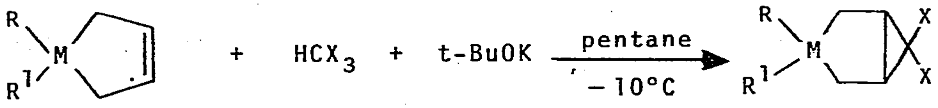
A variety of new diorganogermanium intermediates have been characterized and their condensation reactions with 2,3-dimethylbutadiene used in the synthesis of cyclic germanium compounds (15, 41, 42).





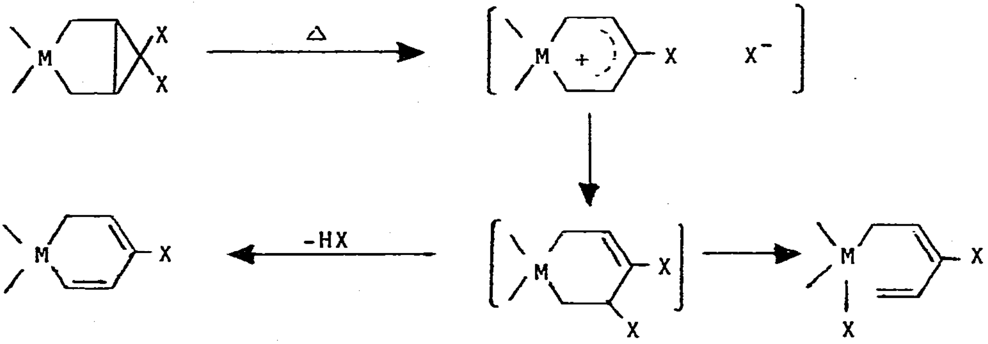
(Ref. 15)

Mazerolles et al. investigated the reaction of dihalocarbenes with various 1-sila- and 1-germa-cyclopent-3-enes and observed the formation of corresponding 6,6-dihalogeno-3-sila- and 3-germabicyclo[3.1.0] hexanes (109).



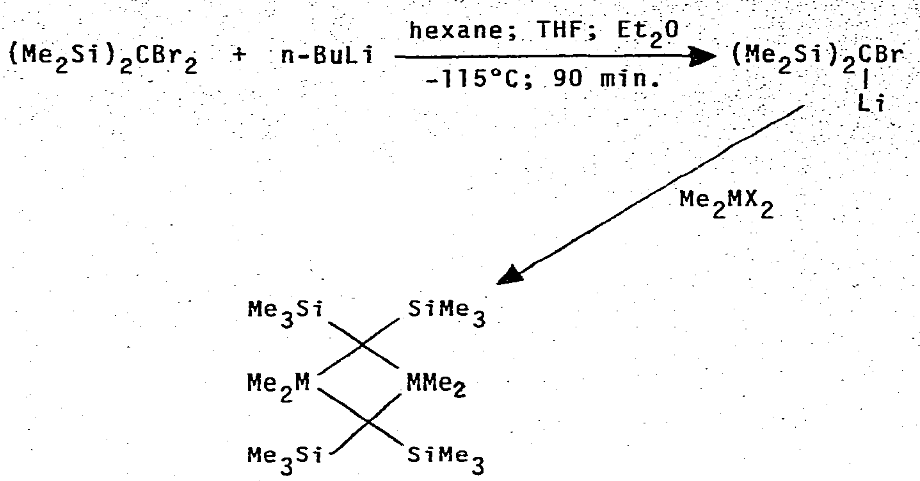
(M = Si, Ge; X = Cl, Br; R = Me, R^1 = Ph)

The thermal instability of these bridged compounds is dependent upon the heteroatom, its substituents and the halogen. Cyclic and linear dienes of silicon and germanium are produced in the decomposition process:

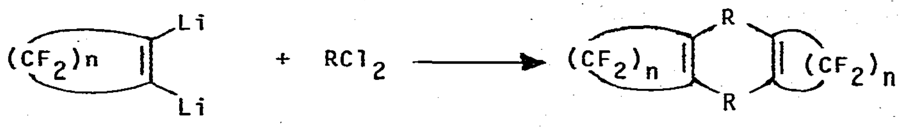


(M = Si, Ge; X = Cl, Br)

A new route to highly substituted 1,3-disila- and digermacyclobutanes has been reported (110):

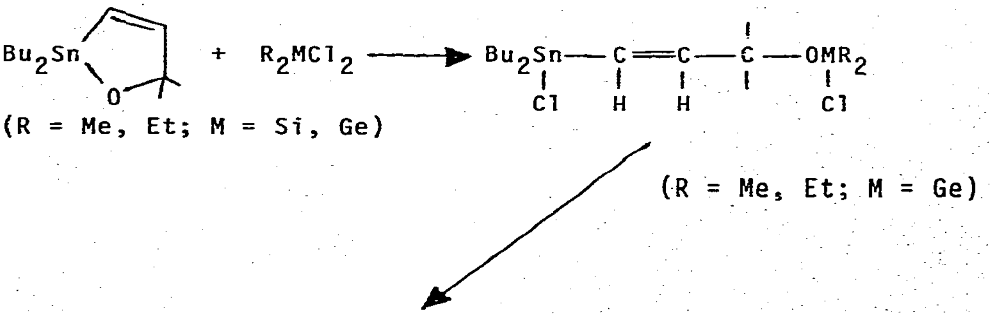


The organometallic derivatives of perfluorocycloalkenes could be synthesized according to the reaction scheme (111):



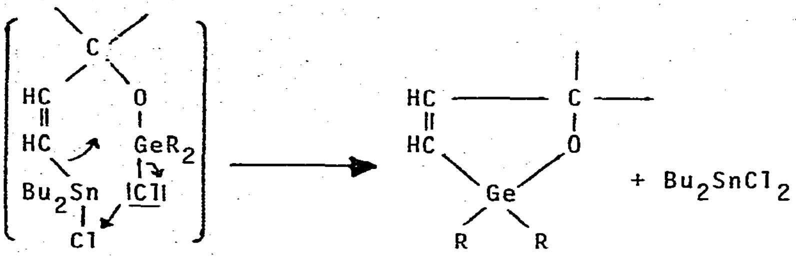
(R = Me$_2$Ge, Me$_2$Sn, PhP, MeAs, n = 2; R = Hg, n = 2, 3, 4)

A number of publications regarding the syntheses of oxygen (112-114) and phosphorus (72) containing germacyclanes have appeared. Some of the results reported are summarized in Chart 12.

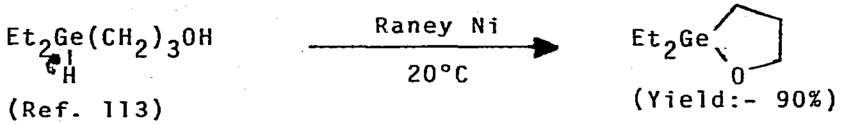


(R = Me, Et; M = Si, Ge)

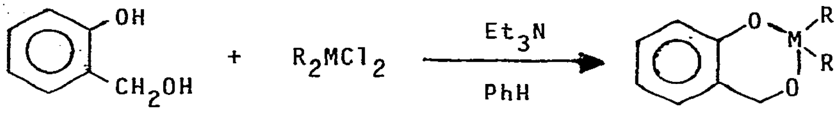
(R = Me, Et; M = Ge)



(Ref. 112)

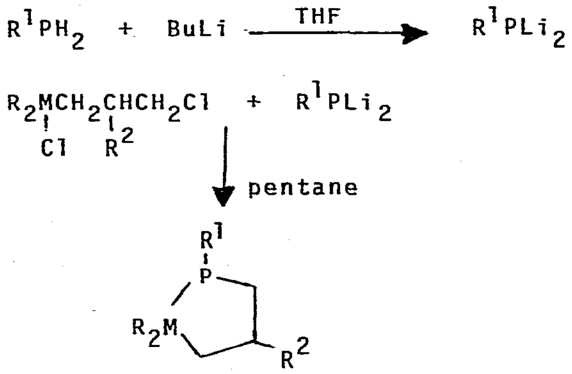


(Ref. 113)



(R = Me, Bu, Ph; M = Si, Ge; yield:- 70-90%)

(Ref. 114)

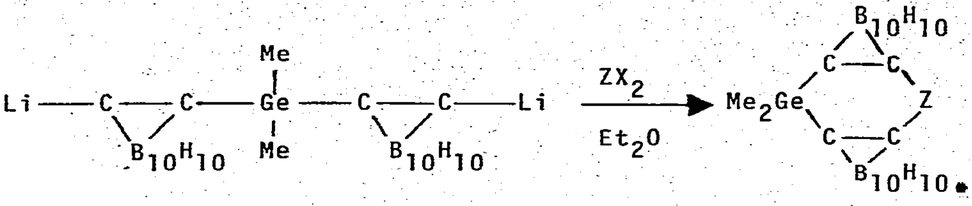


(R^1 = Bu, Ph; R_2 = Me_2, PhMe, Et_2, R^2 = H, Me; M = Si, Ge, Sn)

Chart 12. Synthesis of some germacyclanes

A review article on cycloalkanes containing heterocyclic germanium, tin and lead has appeared (115).

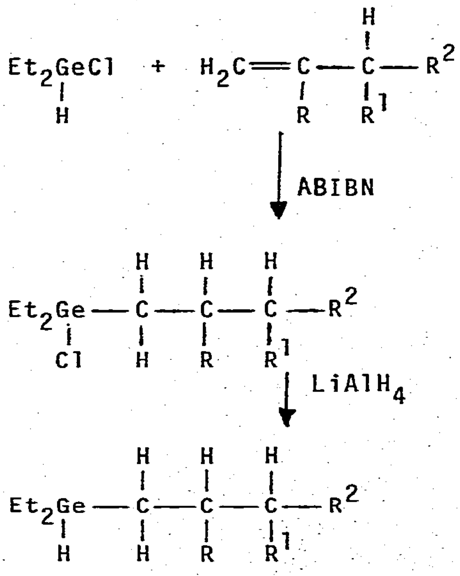
Zakharkin and Shemyakin synthesized six-membered cyclic compounds in which two o-carborane nuclei and two different hetero atoms take part in the formation of the ring (116).

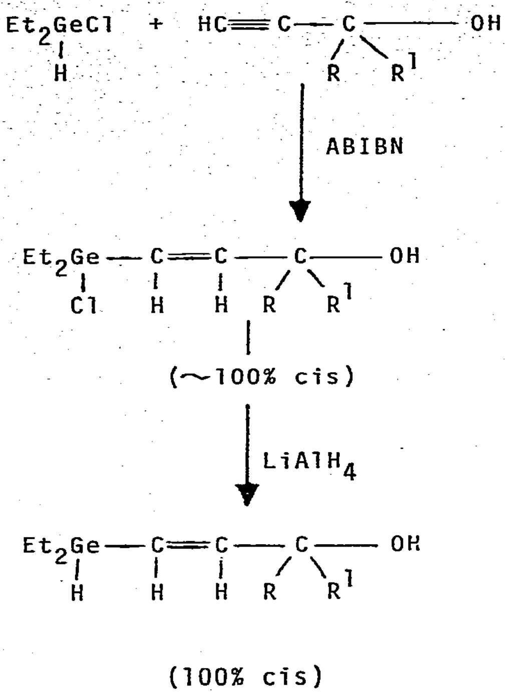


(Z = Me_2Sn, PhP, MeAs)

Carbon-functional germanium compounds

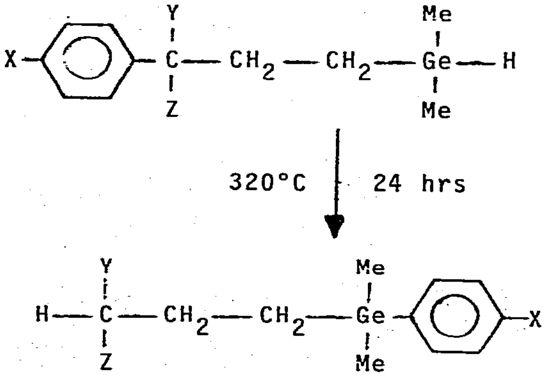
The preparation of some γ-hydroxy-metal hydrides has been achieved according to the reaction schemes (113):





(R = R^1 = H, Me; R = Me, R^1 = H; R = H, R^1 = Me; R^2 = OH, OCOMe, ABIBN = azobisisobutyronitrile)

Sakurai and coworkers reported some novel radical phenyl migrations from carbon to germanium and from germanium to carbon (117):



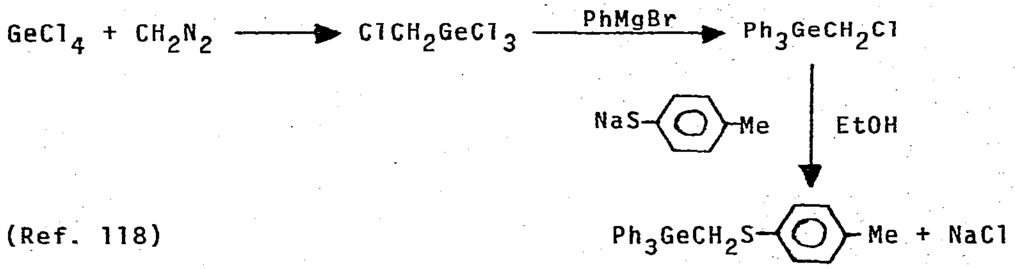
(X = H, Y = Z = Me; X = Y = H, Z = Ph; X = p-Me, Y = Z = Me)

The authors claim it to be the first example of an aryl migration from carbon to germanium.

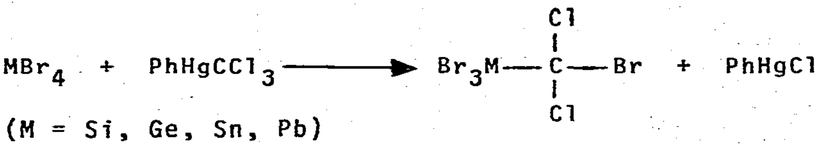
The reactions of halogermanes with a variety of reagents have been used to synthesize carbon-functional germanium compounds (29, 118, 119).

$$\begin{tikzcd} Me_3SiN{=}C{=}NSiMe_3 + 2H_3GeF \arrow[r] & H_3GeN{=}C{=}NGeH_3 + 2Me_3SiF \\ 2Me_3SiCl + Ag_2CN_2 \arrow[u] & \\ CaCN_2 + 2AgNO_3 \arrow[u] & \end{tikzcd}$$

(Ref. 29)



(Ref. 118)



$$MBr_4 + PhHgCCl_3 \longrightarrow Br_3M\text{—}CCl_2\text{—}Br + PhHgCl$$

(M = Si, Ge, Sn, Pb)
(Ref. 119)

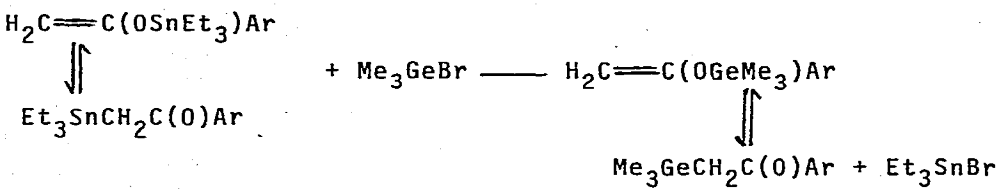
Strom and Jolly prepared the methyl and ethyl esters of 2-germaacetic acid via the reaction (120):

$$H_3GeK + CO_2 \xrightarrow[\text{or triglyme}]{\text{monoglyme}} H_3GeCOOH \xrightarrow[\text{nium fluoroborate; 0°C}]{\text{trialkyloxo-}} H_3GeCOOR$$

(R = Me or Et)

Hydrolysis and thermal decomposition of these derivatives gave CO, GeH_4 and ROH as the products.

The preparation of tin- and germanium-containing derivatives of acetophenones with various substituents in the aromatic ring and the study of the influence of substituents on the position of elementotropic equilibrium have been reported (121).



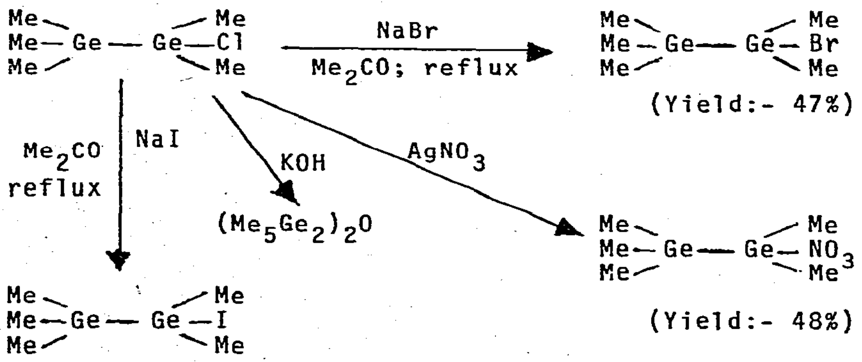
$$\begin{tikzcd} H_2C{=}C(OSnEt_3)Ar \arrow[d, shift left] \arrow[d, leftarrow, shift right] & & \\ Et_3SnCH_2C(O)Ar & + Me_3GeBr \arrow[r, dash] & H_2C{=}C(OGeMe_3)Ar \arrow[d, shift left] \arrow[d, leftarrow, shift right] \\ & & Me_3GeCH_2C(O)Ar + Et_3SnBr \end{tikzcd}$$

(Ar = $p\text{-}ClC_6H_4$, $p\text{-}MeC_6H_4$ etc.)

$$Me_3GeBr + Hg(CH_2COPh)_2 \longrightarrow H_2C{=}C(Ph)OGeMe_3 + Me_3GeCH_2C(O)Ph$$

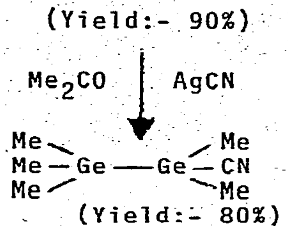
Miscellaneous studies

Andy and Thayer investigated the preparation and properties of some pentamethyldigermyl compounds (122).



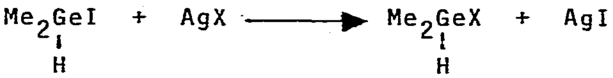
(Yield:- 47%)

(Yield:- 48%)



A review article on the biological aspects and effects displayed by organic compounds of metals and metalloids (including those of germanium) (123) and a publication on the toxicology of germanium hydride (124) have appeared.

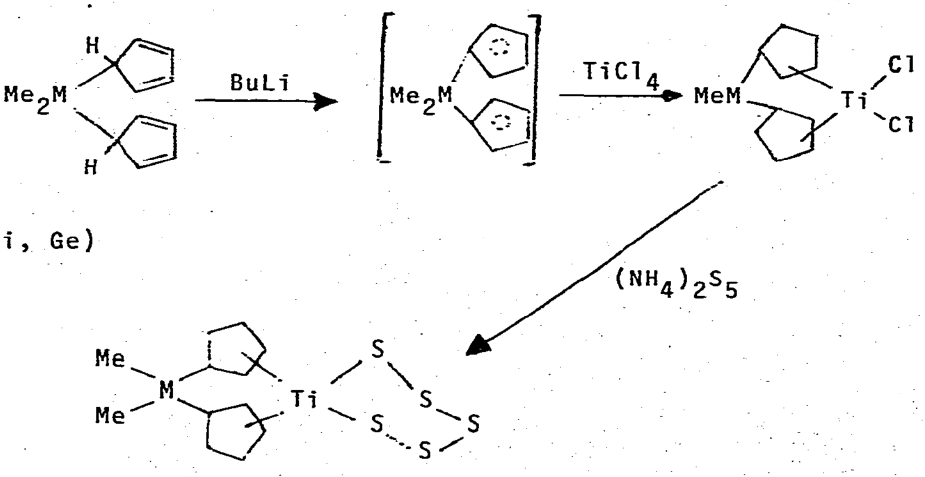
Various reactions which provide convenient routes to a number of organogermanium compounds have been reported (33, 125-129). Some of these are summarized in Chart 13.



$$\underset{\mathrm{H}}{\mathrm{Me_2GeI}} + \mathrm{AgX} \longrightarrow \underset{\mathrm{H}}{\mathrm{Me_2GeX}} + \mathrm{AgI}$$

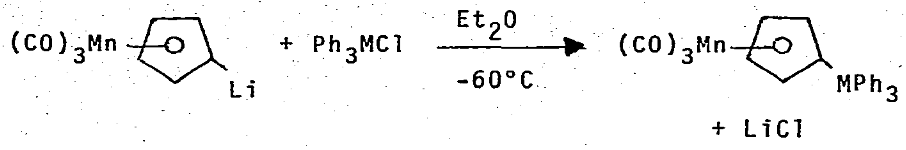
(X = CN, NCO, NCS, OAc)

(Ref. 33)



(M = Si, Ge)

(Ref. 125)



(M = Si, Ge, Pb)
(Ref. 126)

$$Ph_3MCOOH + Ph_2SnH_2 \xrightarrow{Et_2O} Ph_4Sn_2(OOCMPh_3)_2$$

(M = Si, Ge)

Chart 13. Synthetic routes to miscellaneous organogermanium compounds.

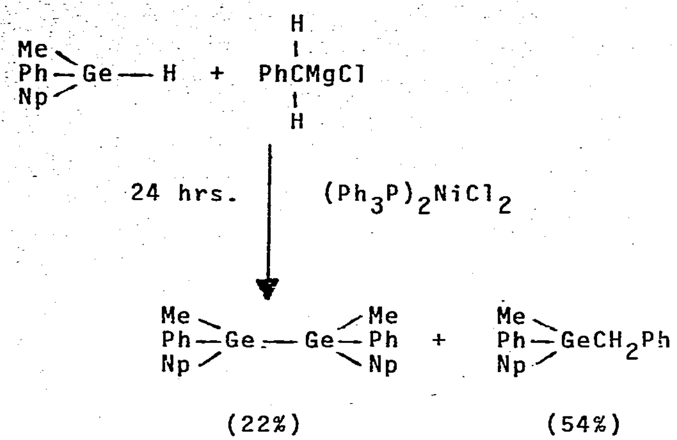
Physico-chemical investigations

A review article on the thermochemistry of organometallic compounds including those of germanium has appeared (130). The vapor pressure, surface tension, viscosity etc. for derivatives of the type R_4Ge (where R = Me, Et, Pr, Bu etc.) (131) and viscosities, densities etc. for a variety of tetraalkyl-, trialkylhydro- and hexaalkyldi-Group IV compounds (132) have been reported. Karapet'yants and coworkers calculated the temperature dependence of saturated vapor pressure of phenyltrichlorogermane (133) and of compounds of the type, $(R_3Ge)_2Hg$ (where R = Et, i-Pr) (134). Thermodynamic data have been derived for some germanium hydride derivatives (135) and for tetraphenylgermane and hexaphenyldigermane (136). Dudorov and Zorin studied the oxidation of germane by oxygen and derived a rate equation for calculating the initial reaction rate (137-141).

The pyrolysis of compounds of the type R_3MH (where M = Si, Ge) has been reported (142). A study of the γ-ray radiolysis of monogermane in the gas phase has been the topic of a Ph.D. thesis (143).

The dipole moments of compounds of the four series $PhSMMe_3$, m- and p-$ClC_6H_4SMMe_3$ and $(Me_3M)_2S$ (where M = C, Si, Ge, Sn, Pb) have been measured. From these data, the $C\hat{S}M$ and $M\hat{S}M$ bond angles and the $\mu[Me_3M-S]$ group moments have been estimated. The bond angles increase significantly from Ph_2S to the compounds of the series $PhSMMe_3$ and $(Me_3M)_2S$ (144). Ramalingam and Soundararajan evaluated the formal charge distribution in, and the electric dipole moment of, a few simple organogermanium compounds. The difference between the experimental and calculated moments in the case of alkylhalogermanes is explained in terms of the $p_\pi - d_\pi$ back bonding effect outweighing the electron releasing effect (145). The determination of the electric dipole moments of gaseous H_3GeX (where X = Cl, Br, I) and $MeGeCl_3$ has been accomplished by using microwave nonresonant absorption of vapors and (or) dielectric constant measurements (146).

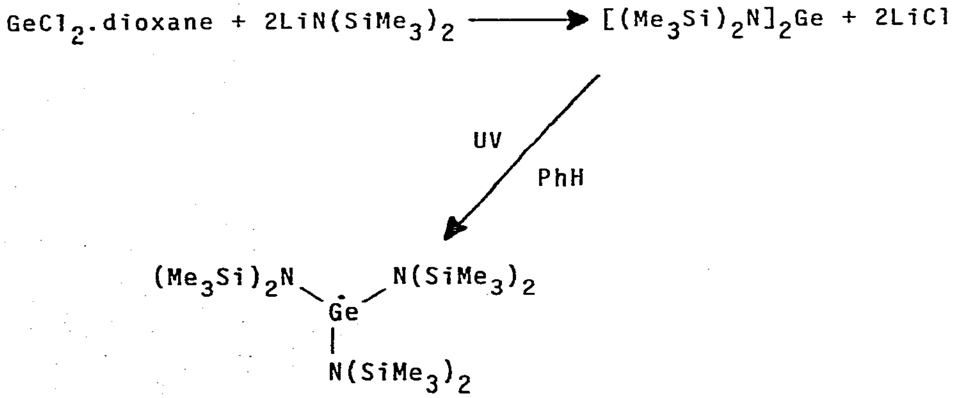
Carré and Corriu obtained an optically active digermane via the reaction (147, 148):



(Np - naphthyl)

The reactions of organolithium and Grignard reagents with optically active alkoxygermanes (149) and the stereochemistry of nucleophilic substitution of chloro- and alkoxy-germanes by germyllithium reagents have been reported (150).

Lappert and coworkers reported a general photochemical procedure for the synthesis of Group IV metal-centered radicals and their esr characterization (151):



The rates of cleavage by aqueous methanolic alkali have been measured for the C-MR_3 bonds in some arenechromium tricarbonyl complexes. The relative rates for the complexes $(h^6\text{-}XC_6H_4\text{-}C{\equiv}CGeEt_3)Cr(CO)_3$ with varying X correlate excellently with those for the uncomplexed $XC_6H_4C{\equiv}CGeEt_3$ compounds, showing that the $Cr(CO)_3$ group causes no distortion of the pattern of substituent effects, but the groups X (m-CF_3, H, p-OMe etc.) have a smaller influence on the rate in the complexed series (152). An excellent review on the kinetics and the mechanisms of the reactions of silicon and germanium with halogens, their hydrides and organic derivatives has appeared (153).

Some other studies include: σ_p constants of some substituted silyl and germyl groups (154); equilibrium distributions (155) and equilibrium constants (156) for the scrambling of various pairs of substituents in organosilicon and germanium compounds; kinetics of the abstraction of hydrogen from Group IV methyls by trifluoromethyl and methyl-d_3 radicals (157); hyperconjugation in allyl and benzyl derivatives of Group IV elements (158); determination of the energy of electronic transition in $R_3\hat{M}OM'R_3$ (where R = Me, Et; M, M' = C, Si, Ge, Sn; X = O, S) type derivatives (159); CNDO/2 calculations (160) and the calculation of valence local orbitals of the ground states (161) of some germanium compounds; new anion, thermal and radical rearrangements in organo-silicon and -germanium chemistry (162); reaction of hydrogen atoms with silanes and germanes (163) and determination of dissociation constants of chlorine containing organogermanium compounds in methanol and ethanol (164).

Spectral studies

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

Infrared and Raman studies

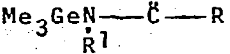
The UV-photolysis of germane and some mixed halogermanes in argon and carbon monoxide have been performed between 4°K and 24°K. The results of these experiments support the successful isolation and characterization of a variety of germanium containing free-radical species produced as a result of primary and secondary photolytic processes (165).

The infrared and Raman spectra of (thioacetoxythio)-trimethyl-Group IV metals [RCS_2MMe_3 derivatives] have been recorded. The results indicate that intramolecular coordination of the thiocarbonyl sulfur to Group IV metal is small or negligible (166).

Drake and coworkers reported the infrared and Raman spectra of the methylgermanium fluorides of the type Me_nGeF_{4-n} (where n = 1, 2, 3). The fundamental frequencies for each molecule were assigned and supported by normal coordinate analyses based on a modified valence force field (167).

The infrared intensities have been determined for the carbonyl stretching vibrations of molecules of the type $X_3MMn(CO)_5$ (where M = Si, Ge, Sn; X = Cl, Br. I). The relation between the infrared intensities and the metal-metal stretching force constants may be interpreted in terms of the interaction of the M-Mn σ-orbitals with the σ^* orbitals of the carbonyl groups (168). Onaka reported the infrared spectra of $Me_3GeMn(CO)_5$ and normal coordinate analyses were made for $Me_3GeMn(CO)_5$ and $H_3GeMn(CO)_5$ on the basis of a modified Urey-Bradley force-field. The degree of the π-interaction between the Group IV metal and manganese atoms and the strength of the metal-metal interaction were controlled by ligands on Group IV metal atom (169).

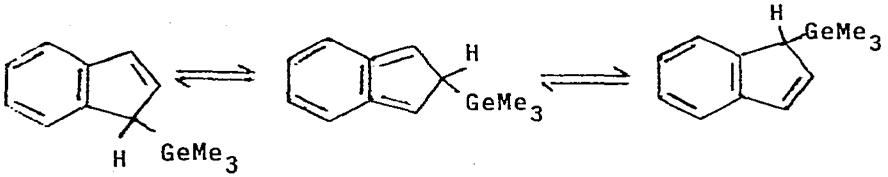
It has been shown that swelling of polyethylene cuvettes during measurements of infrared spectra of organic compounds of silicon, germanium and lead in the region 10-500 cm^{-1} considerably affect the obtained spectra due to a band at 329 cm^{-1}. These cuvettes are suitable for short-term infrared studies of these compounds (170).

More specific studies include the following compounds: chlorophenyltrichlorogermanes (14); $(C_3H_5)_4M$ (M = Si, Ge, Sn) (171); Me_4M (M = C, Si, Ge, Sn) (172); benzothioazoledichlorogermylene (31); pentafluorophenylgermanium hydrides (32); H_3GeCH_2Br and D_3GeCH_2Br (173); $HGeCl_3$ and $DGeCl_3$ (174); solid phases of GeH_4 (175); triorganogermanes (176); germanium-boron bonded derivatives (46-48); germanium-iron bonded compounds (52, 54, 177, 178); $X_3M'M(CO)_5$ (X = Me, Cl; M' = Ge, Sn; M = Mn, Re) (179); $Cl_3GeFe(CO)_4^{\ominus}$ (180); $X_3MCo(CO)_4$ (M = C, Ge; X = H, D, F) (181); $Ph_3MCo(CO)_3PPh_3$ (56); $C_5H_5Co(NO)MI_3$ (where M = Ge, Sn) (57); $Me_3GeCo(CO)_4$ (58); germanium-ruthenium complexes (61, 62, 64);  $Me_3Ge\underset{R^1}{N}-\overset{O}{\overset{\|}{C}}-R$ (where R = H, Me; R^1 = H, aryl) (66); trimethylgermylphosphines (71); $Me_3GeX(CF_3)_2$ (where X = P, As) (182); $(Me_3M)_3SbNi(CO)_3$ (where M = C, Si, Ge, Sn) (76); iminoxyorganogermanes (78); sulfinic acid derivatives of germanium

(83-85); mixed silicon-germanium peroxides (89); pentafluro-phenylgermyl-chalcogens (92); $Ph_4Ge_4S_6$ (93); $H_3GeSeMe$, $Me_2\underset{H}{Ge}SeMe$ etc. (183); $M_2(CH{=}CH_2)_6$ (M = Si, Ge, Sn) (97); oxametallacycloalkanes (113); 1-oxa-2-germacyclo-pentenes and -pentanes (184); $H_3GeCOOR$ (R = Me, Et) (120); $Ph_4Sn_2(OOCMPh_3)_2$ (where M = C, Si, Ge) (129); germyl-allene compounds (185).

Nuclear Magnetic Resonance Studies

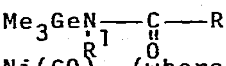
The ^1H- and ^{13}C-NMR spectra of the fluxional molecules $C_9H_7MMe_3$ (where M = Si, Ge, Sn) have been studied over a wide range of temperatures. The metal atom in the indenylgermane migrates through a 1,2-shift (186):



Analogous spectral analysis of 3,5-dimethylpyrazole substituted at the nitrogen has been performed over a wide range of temperatures (187). In the pyrazole compounds germanium migrates faster than silicon as in the cyclopentadienyl and indenyl series. An excellent review article on fluxional main Group IV organometallic derivatives has appeared (188).

It has been reported that ^{13}C-chemical shift variations within a series of phenyl, furyl and thienyl organometallics are best understood in terms of alkyl and aryl substituent effects on ^{13}C-chemical shifts and not variations in d_π-p_π metal-aryl interactions (189).

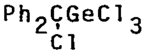
MacLean and Sacher reported proton NMR chemical shifts for germanium acetylides of the type $Me_nGe(C{\equiv}CH)_{4-n}$ (where $n = 0-3$) (190).

More specific studies include the following compounds: D_3CGeH_3 and H_3CGeD_3 (191); germanium-hydrogen derivatives (33, 34, 192); ^{13}C-chemical shifts of phenyltrimethylgermane (193); germanium-mercury bonded compounds and their reactions (194); germanium-boron bonded derivatives (45-48); $[(\eta^5-C_5H_5)Fe(CO)CNMe]R$ (where R = Me_2GeCl, Me_3Sn etc.) (52); NMR studies of ^{73}Ge (195); germanium-ruthenium complexes (61-63);  $Me_3Ge\underset{R^1}{N}—\underset{\overset{\|}{O}}{C}—R$ (where R = H, Me; R^1 = H, aryl) (66); $(Me_3M)_3SbNi(CO)_3$ (where M = C, Si, Ge, Sn) (76); organo(oxinato)germanes (77); sulfinic acid derivatives of germanium (83-85); $Ge_2(CH{=}CH_2)_6$ (97); germa-bicyclohexanes (109); oxametallacycloalkanes (113); germacyclanes containing o-carborane nuclei (116); $Ph_3GeCH_2SC_6H_4Me$-p (118); $H_3GeCOOR$ (where R = Me or Et) (120); pentamethyldigermyl compounds (122); germanium-iron bonded derivatives (177, 178); methylseleno-derivatives of germanium hydrides (183); organogermanium acetylacetonate complexes (196) and cyclopentadienyl metal compounds (197).

Mass Spectroscopic studies

A comparison of the ionization energies of $PhSMMe_3$ (where M = C, Si, Ge, Sn, Pb) with those of Me_4M compounds shows that the absolute values are lower and in a narrower range in the former series (198).

Clark and Rake reported the mass spectra of systems containing Group IV-transition metal bond eg. $Ph_{3-n}(C_6F_5)_nMMn(CO)_5$ (where M = Si, Ge, Sn; n = 0-3). In all cases the initial fragmentation is by the loss of one or more carbonyl groups from the molecular ion, followed by the cleavage of the metal-metal bond (199).

Mass spectroscopic data have been reported for the following compounds: Cl_3CGeCl_3, $ClCH_2GeCl_3$ and  $Ph_2\underset{Cl}{C}GeCl_3$ (200); fluoroaromatic heterocyclic derivatives of Si, Ge, Sn (201); germacyclopentenes (202); Me_4M (where M = Si, Ge, Sn, Pb) (203); germyladamantane (25); some germanium-boron bonded derivatives (45, 46); $C_5H_5Co(NO)MI_3$ (where M = Ge, Sn) (57); $Me_3GeCo(CO)_4$ (58); $Ge[N(SiMe_3)(CMe_3)]_2$ (68); heterocyclic silicon and germanium compounds of α-hydroxybenzyl alcohol (114); $Ph_3GeCH_2SC_6H_4Me$-p (118); pentamethyldigermyl compounds (122) and $H_3GeCOOR$ (where R = Me or Et) (120).

Miscellaneous

Some general articles dealing with the spectroscopy of organometallic compounds have appeared (204-206).

The electron spin resonance spectra for a series of organometal-substituted benzenes have been reported (207,208).

The core electron binding energies for MX_4 (where M = C, Si, Ge; X = H, F, Cl) type compounds have been measured by X-ray photoelectron spectroscopy in the gas phase (209). The He(I) photoelectron spectra have been obtained for Me_3MPh and Me_3MCH_2Ph (where M = Group IV metal) (210) and for compounds of the type R_4M (where R = Me_3SiCH_2, M = Ge, Sn) (211). Some other articles on photoelectron spectroscopy of organometallic compounds (including those of germanium) have appeared (212-215).

The solution ultraviolet spectra for p-trimethyl-silyl and -germyl-N,N-dimethylaniline in acetonitrile and pentane have been reported. The Group IV substituents perturb the excited states to a much larger extent than the ground states (216).

Some other studies and articles include: NQR spectra of trimethylgermyl perrhenate (217); ^{59}Co-NQR spectra for $XCo(CO)_3L$ and $XCo(CO)_2L_2$ (where X = Ph_3Sn or other similar Group IV metal derivative; L = Bu_3P, $P(OMe)_3$ etc.) (218); microwave spectrum of (fluoromethyl)germane (219); microwave spectrum of Me_3GeCN (220); molecular structure of dichloro- and dibromo-germane by gas-phase electron diffraction (221); spectroscopic studies on some Group IV-Mn and -Fe metal-metal bonds (222); normal vibrations of tetrahedral, XY_4 hydrides (223); frequencies of Ge-H stretching modes in organogermanes (224); core electron spectra of some germanium compounds (225); internuclear bond distances and electronegativities in YXH_3 and HXY_3 (where X = C, Si, Ge; Y = F, Cl, Br, I) molecules (226); calculation of empirical linear relations between bond dissociation energies and interatomic distances for the R-X bond (X = F, Cl, Br, I; R = Me, Ph, X_3Ge etc.) (227); calculation of force and rotational constants of halogermanes (228); Urey-Bradley force constants for H_2YX_2 (Y = C, Si, Ge; X = F, Cl, Br) type molecules (229); force fields of $X_3MCo(CO)_4$ (M = Si, Ge, Sn; X = H, D, F, Cl etc.) (230); prediction of the frequencies of normal vibrations of MDX_3 (where M = C, Si, Ge; X = Cl, Br, I) type molecules (231); correlation of basicities and substituent constants of oxygen-containing organic compounds via infrared data (232) and the nature of angular force coefficients of polyatomic molecules (233).

The reports regarding structural data for various organogermanium compounds include the crystal structures of $(C_6F_5)_4Ge$ (234); $Ph_3GeSC_6H_4$-t-Bu-p (235) and $Cl_3GeCo(CO)_4$ (236).

Analysis and Applications

The gas-chromatographic separation of fluorinated organogermanes has been reported (237) and a technique for separating germane from mixtures has been patented (238).

Dobronevskaya et al. outlined a variety of methods for the determination of organohalogermanes (239-241). A review article on the elemental and functional methods for analyzing organo-silicon, -germanium, -tin etc. compounds has appeared (242). Shanina and coworkers reported a method for quantitative analysis of heteroorganic compounds (243).

A review article on application possibilities of germanium and its derivatives in organic and biochemistry has appeared (244). Various claims regarding applications of organogermanium compounds include: Et_4Ge as radioactive tracer in the process of gasoline distillation (245); organogermaniums of the type R_3GeX (R = alkyl, X = OH, halogen etc.) or $(R_3Ge)_2Y$ (Y = O, S) as active component against caries hence their use in toothpaste, mouthwashes etc. (246); treatment of hypertension with germanium sesquioxide derivatives (247, 248); stabilizing influence of Ph_3MNCO (where M = C, Si, Ge, Sn, Pb) on PVC during thermal degradation (249); in the preparation of block copolymers (250); preparation of linear polyesters with good whiteness in the presence of organogermanium halides (251) and the use of volatile hydrides for the synthesis of high temperature superconducting phases in the Nb-Ge and V-Ge etc. systems (252).

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