GERMANIUM

ANNUAL SURVEY COVERING THE YEAR 1972

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Books and reviews

Apart from the Annual Survey covering the year 1970 (1), two review articles covering the literature between the period 1969-70 on the organic compounds of germanium (2) and the chemistry of both inorganic and organic derivatives of germanium, tin and lead (3) have appeared. The literature on inorganic, organic and organometallic compounds containing elements of Groups I-VIII for the year 1971 has been surveyed (4). Few other general articles (5-7) which also include some 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

Zueva et al. continued their investigations (see AS70; 205 and AS71; 126) on the direct synthesis of lower trialkylhalogermanes and studied (8) the effect of di- and tri-valent elements (Mg, Zn, Al Ga etc.) on the yield and preferential formation of trimethylchlorogermane. The optimum conditions:

$$\underset{(20\%)}{\mathrm{Ge + Cu + Ga}} + \mathrm{MeCl} \xrightarrow[5\mathrm{hr}]{400^{\circ}} \underset{(85\%)}{\mathrm{Me_3GeCl}} + \underset{(10\%)}{\mathrm{Me_2GeCl_2}} + \underset{(5\%)}{\mathrm{MeGeCl_3}}$$

Aluminium and gallium have also been used in the direct synthesis reactions of germanium with MeBr, MeI, EtCl and other alkyl halides. In almost all these cases, in the presence of these metals, together with dialkyldihalogermane and alkyltrihalogermanes, trialkylhalogermanes are also obtained.

The direct synthesis of some pentafluorophenyl derivatives of germanium has been achieved by the reaction (9):

$$\mathrm{C_6F_5Br} + \underset{(60/40\%)}{\mathrm{Ge/Cu}} \longrightarrow \mathrm{C_6F_5GeBr_3} + \mathrm{(C_6F_5)_2GeBr_2}$$

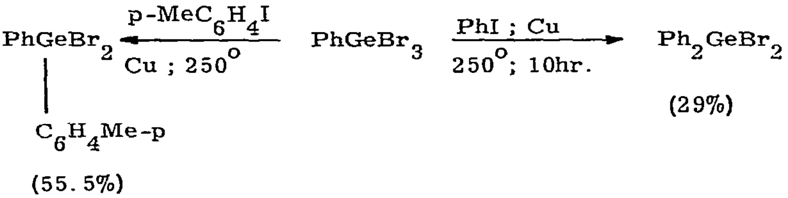
A number of organotrihalogermanes have been prepared by the reaction between organic halides and germanium tetrahalides (10, 11) in the presence of a metal in an inert atmosphere:

$$\mathrm{GeX_4} + \mathrm{RX} \xrightarrow[140^{\circ};\ 5\mathrm{hr.}]{\mathrm{Cu}} \mathrm{RGeX_3}$$

($R = n-C_4H_9$, C_7H_{15} ; $X = Br, I$; yield:- 45 - 59%)

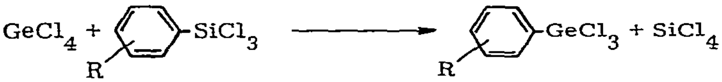
$$GeBr_4 + PhBr \xrightarrow[200^\circ;\ 16\ hr.]{Cu;\ sealed\ tube} \underset{(50.6\%)}{PhGeBr_3}$$

Further arylation leads to the synthesis of diorganodihalogermanes (12):



$$\underset{\underset{(55.5\%)}{C_6H_4Me\text{-}p}}{PhGeBr_2} \xleftarrow[Cu\ ;\ 250^\circ]{p\text{-}MeC_6H_4I} PhGeBr_3 \xrightarrow[250^\circ;\ 10hr.]{PhI\ ;\ Cu} \underset{(29\%)}{Ph_2GeBr_2}$$

Another synthetic route to aryltrichlorogermanes involves the reaction of germanium tetrachloride with an aryltrichlorosilane in the presence of a Lewis acid-type catalyst with simultaneous distillation of the silicon tetrachloride formed (13):



($R = H, Me, Cl$)

Kolesnikov et al. observed an easy insertion of $GeCl_2$: (generated from its dioxane complex) into carbon-halogen bonds of different polychloromethanes alkyl chlorides and aryl halides (14):

$$GeCl_2 : + RX \longrightarrow RGeCl_2X$$

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

Depending upon the nature of R, the reaction is carried out either at the reflux temperature of RX or in an autoclave at 120 - 250° for 6 - 25 hrs The yields of the final products also vary from 14 - 90%, again depending upon the nature of R.

In contrast to the polychloromethanes, the polychloroethanes reacted as:

$$GeCl_2 : + Cl_3CCCl_3 \xrightarrow[5\text{-}16hr.]{130^\circ} Cl_3CCCl_2GeCl_3 \xrightarrow{\Delta} GeCl_4 + Cl_2C = CCl_2$$

A convenient route to germanium dibromide and some other bromogermanes has been reported (15):

$$\mathrm{Ge + Br_2 \xrightarrow{350^o} \underset{(38\%)}{GeBr_2} + \underset{(39\%)}{GeBr_4}}$$

$$\mathrm{Ge + GeBr_4 \xrightarrow{400^o} \underset{(51\%)}{2GeBr_2}}$$

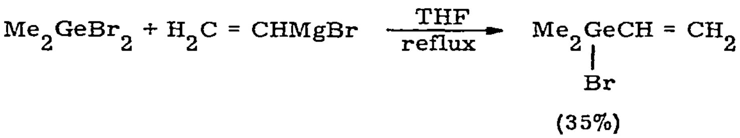
$$\mathrm{\underset{(30\%)}{Br_3GeCBr_3} \xleftarrow[reflux]{CBr_4;\ PhMe} GeBr_2 \overset{GeBr_4\ ;\ PhMe}{\underset{reflux}{\rightleftarrows}} \underset{(25\%)}{Br_3GeGeBr_3}}$$

The preparation and properties of germanium-halogen bond havebeen reviewed (16).

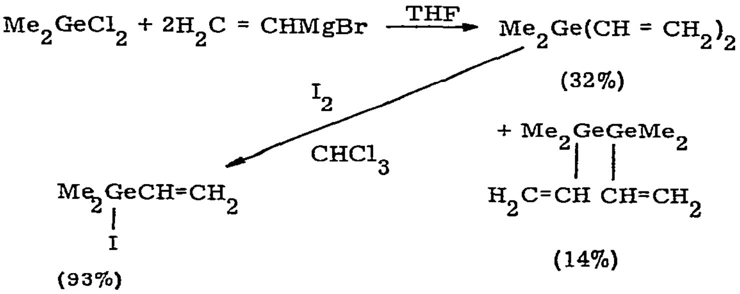
Alkylation and arylation

The application of Grignard reagents in the preparation of organometallic and organometalloid compounds has been reviewed (17).

Curtis and Job reported the synthesis of some dimethylvinylhalogermanes by the conventional Grignard procedure (18):



$$\mathrm{Me_2GeBr_2 + H_2C = CHMgBr \xrightarrow[reflux]{THF} \underset{(35\%)}{Me_2\underset{Br}{\underset{|}{Ge}}CH = CH_2}}$$



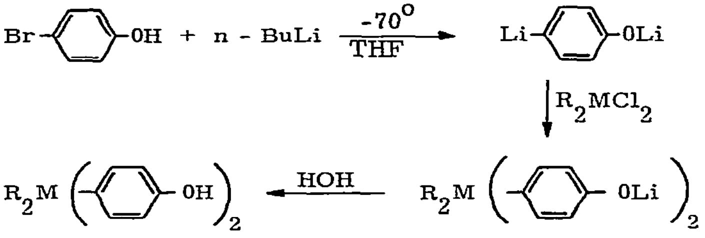
$$\mathrm{Me_2GeCl_2 + 2H_2C = CHMgBr \xrightarrow{THF} \underset{(32\%)}{Me_2Ge(CH = CH_2)_2} + \underset{(14\%)}{Me_2\underset{H_2C=CH}{\underset{|}{Ge}}\underset{CH=CH_2}{\underset{|}{Ge}}Me_2}}$$

$$\mathrm{Me_2Ge(CH = CH_2)_2 \xrightarrow[CHCl_3]{I_2} \underset{(93\%)}{Me_2\underset{I}{\underset{|}{Ge}}CH=CH_2}}$$

The authors also claim to have obtained yields in the excess of 90% for tetramethylgermane in the reaction:

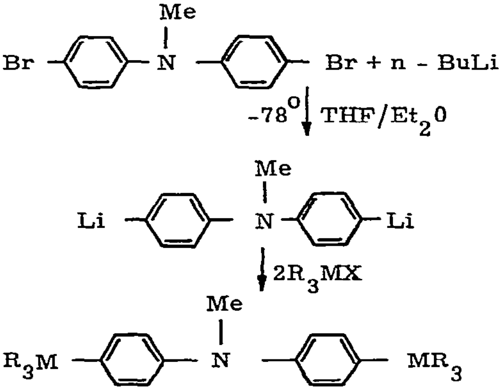
$GeCl_4 + 4MeMgBr \longrightarrow Me_4Ge + 4MgBrCl$ by replacing relatively expensive dibutyl ether (see AS70; 206) with xylene.

Organometallic bis(p-hydroxyphenyl) derivatives of Group IVB elements could be synthesized according to the reaction (19):



(R = Me, Ph; M = Si, Ge, Sn, Pb; yield:- 55 - 80%)

Some p-disubstituted organometallic derivatives of diphenyl - N - methylamine have been synthesized according to the reaction scheme (20):



(R = Me, Ph; X = Cl, Br; M = Si, Ge, Sn, Pb; yield:- 48 - 66%)

Germanium - hydrogen compounds

A very thorough account of the chemistry of the hydrides of the elements of main Groups I - IV has been the subject of a book by Wiberg and Amberger (21).

The reduction of germanium and tin tetrahalides with lithium aluminium hydride in diethyl ether, tetrahydrofuran or dioxane has been shown to bear a stepwise character, with the formation in the first step of the intermediate trihalogermanes or trihalostannanes which are bonded to the ether in the comple This step is followed by the reduction of the complexes, the nature of which is responsible for the low yields of germane and stannane (22). On the other hand germanium tetrachloride could be reduced to germane by using diisobutyl aluminium hydride (23, 24):

$$GeCl_4 + 6\,i\text{-}Bu_2AlH \longrightarrow \underset{(60\%)}{GeH_4} + \underset{(\text{minor amounts})}{GeHCl_3 + Ge_2H_6}$$

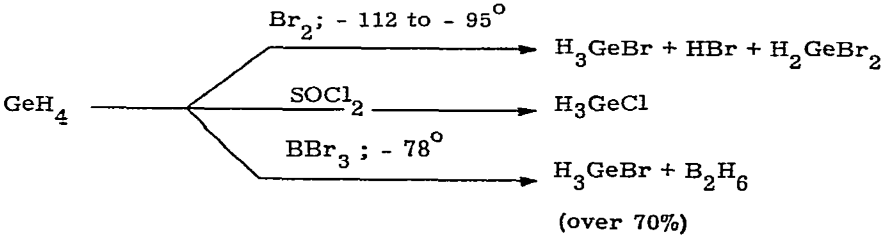
Nametkin et al. observed that mono- and di-organosilicon hydrides can reduc germanium tetrachloride to trichlorogermane (25):

$$GeCl_4 + R_2SiH_2 \xrightarrow[Et_2O;\ 4\text{-}10hr]{\text{room temp.}} \underset{(80\%)}{HGeCl_3.2Et_2O} + R_2SiHCl$$

(R = Me, Et, Pr, Ph)

Catalytic amounts of $Et_3N.HCl$, $Me_4\overset{+}{N}\overset{-}{Cl}$ and $Et_4\overset{+}{N}\overset{-}{Cl}$ greatly accelerated the rate of formation of $HGeCl_3.2Et_2O$. Small amounts of $HGeCl_3.2Et_2O$ itself readily catalyzed hydrogen - halogen exchange in the reaction. The present method seems to be a convenient route to the etherate which possesses high reactivity in a number of specific chemical reactions.

The reactions of germane with bromine (26), thionyl chloride (27) and boron tribromide (28) also provide convenient synthetic routes to trihalogermane

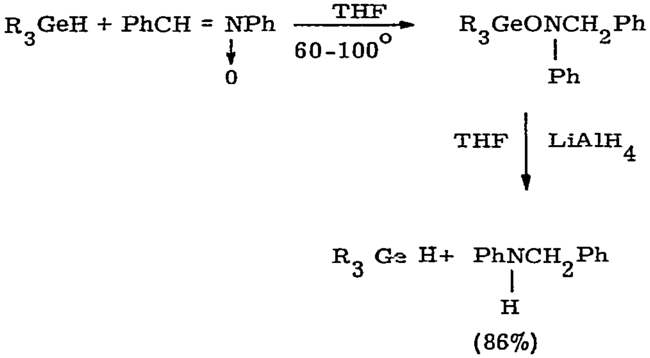


In a review article on reactivity of the germanium-hydrogen compounds the change of polarity of the germanium - hydrogen bond has been discussed and related to the high electronegativity of germanium (29).

Drake and Westwood reviewed the application of discharge techniques to synthesis in inorganic chemistry including the effect of ozonizer - type silent electric discharges on the hydrides and substituted hydrides of the metalloids, B, Si, Ge, P and As (30).

In a study on the scope of the reduction of organic halides with trialkylgermanes under homolytic condition it has been shown that these hydrides reduce polyhaloalkanes without catalysts under mild conditions. The observed orders of reactivity and selectivity in the reduction are consistent with a radical chain mechanism involving free germyl radicals (31).

The 1, 3-addition of hydrogermanes to α , N-diphenylnitrone has been reported (32):



$$R_3GeH + PhCH = \underset{\substack{\downarrow \\ O}}{N}Ph \xrightarrow[60\text{-}100^{\circ}]{THF} R_3GeO\underset{\substack{| \\ Ph}}{N}CH_2Ph$$

$$\text{THF} \Big\downarrow \text{LiAlH}_4$$

$$R_3GeH + Ph\underset{\substack{| \\ H}}{N}CH_2Ph \quad (86\%)$$

$\left[R_3 = Et_3\ (25\%),\ Ph_3(40\%),\ Ph_2Cl\ (99\%) \right]$

The reactions probably proceed via a radical mechanism as catalytic amounts of azobisisobutyronitrile favour the reactions hereas these are inhibited by the presence of galvinoxyl.

Van Dyke et al. studied the properties of silicon-hydrogen and germanium-hydrogen bonds when they are present in the same molecule (33). The reactions are compiled in Chart 1.

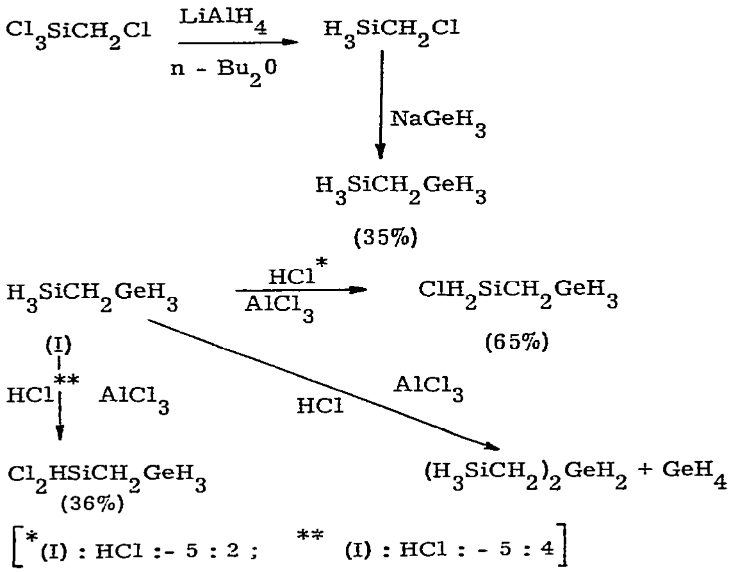


Chart 1. Synthesis and reactions of silylgermylmethane.

Thus the interaction with gaseous hydrogen chloride in the presence of aluminium trichloride leads to predominant substitution on the silicon rather than germanium. The substitution is somewhat unexpected based on the fact that methylgermane halogenates at room temperature (34, 35) whereas satisfactory halogenation of methylsilane requires temperatures of about 100^o (36).

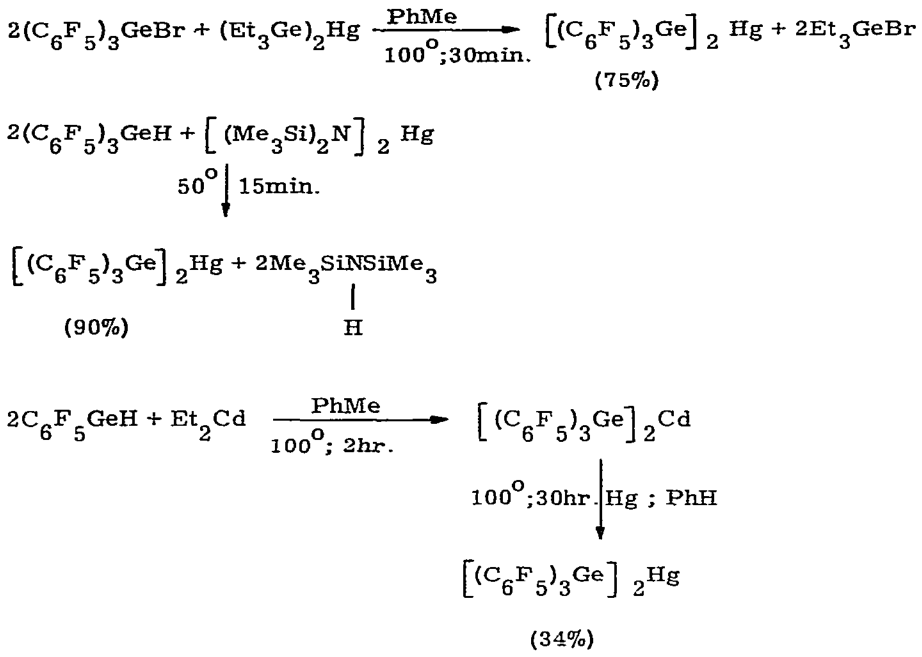
Germanium - metal compounds

The methods of preparing organosilyl- and organogermyl- mercury derivatives and their application in the syntheses of organometallic compounds of silicon and germanium have been reviewed (37).

Vyazankin and coworkers reported various synthetic routes to germyl-cadmium and -mercury derivatives containing pentafluorophenyl fragments (38) These are summarized in Chart 2.

$$2(C_6F_5)_3GeH + Et_2Hg \xrightarrow[100^o;\ 2.5hr.]{PhMe} [(C_6F_5)_3Ge]_2\,Hg + 2EtH$$

$$(75\%)$$



$$2(C_6F_5)_3GeBr + (Et_3Ge)_2Hg \xrightarrow[100^{\circ};30min.]{PhMe} [(C_6F_5)_3Ge]_2Hg + 2Et_3GeBr \quad (75\%)$$

$$2(C_6F_5)_3GeH + [(Me_3Si)_2N]_2Hg \xrightarrow{50^{\circ};\ 15min.} [(C_6F_5)_3Ge]_2Hg\ (90\%) + 2Me_3Si\underset{H}{\underset{|}{N}}SiMe_3$$

$$2C_6F_5GeH + Et_2Cd \xrightarrow[100^{\circ};\ 2hr.]{PhMe} [(C_6F_5)_3Ge]_2Cd \xrightarrow[100^{\circ};30hr.]{Hg\ ;\ PhH} [(C_6F_5)_3Ge]_2Hg \quad (34\%)$$

Chart 2. Synthesis of some germyl - cadmium and -mercury compounds.

The radical exchange reactions between bis(triethylgermyl)mercury and bis(polyfluoroalkyl) mercurials have been shown to proceed as (39).

$$(Et_3Ge)_2Hg + R_2Hg \xrightleftharpoons[20\text{-}100^{\circ}]{PhH} 2Et_3GeHgR$$

$$\left[R = CF_3,\ CH_2CF_3,\ CHFCF_3,\ CF_2CF_3,\ CFClCF_3,\ CH(CF_3)_2,\ CF(CF_3)_2;\ \text{yield:- } 63 - 82\%\right]$$

These are thermally stable liquids capable of vacuum distillation. The stability of these derivatives is explained from the assumption that in - Hg - R groupings there exists an intramolecular donor-acceptor interaction F-Hg, which compensates to a certain extent for the electron attraction of R. This effect opposes the radical exchange process and enhances the stability of the compound (Et_3GeHgR) formed. On the other hand, factors which disturb the intramolecular coordination between mercury and fluorine atoms should cause a sharp reduction in the stability of Et_3GeHgR. Indeed, the fluoride ions catalyze the decomposition of fluoroalkyl (triethylgermyl) mercurials in tetrahydrofuran:

$$Et_3GeHgR \xrightarrow[\text{THF}]{\text{CsF}} Et_3GeR + Hg$$

$$\left[R = CF_3,\ CF_2CF_3,\ CFClCF_3,\ CH(CF_3)_2,\ CF(CF_3)_2\right]$$

The exchange reactions of bis(triethylgermyl) mercury with ethyl esters of α-mercurated fluoroacetic acids have been shown to proceed analogously (40):

$$\begin{array}{ll} (Et_3Ge)_2Hg + R_2Hg \xrightarrow[\text{PhMe}]{\text{THF or}} & 2Et_3GeHgR \\ & \quad\downarrow \\ & 2Et_3GeR + 2Hg \end{array}$$

$$\left[R = CHFCOOEt,\ CF_2COOEt,\ CFClCOOEt\right]$$

The equilibrium among the mercurials formed in the reactions of bis(trimethylsilyl) mercury with trialkylmethoxygermanes (41) and the exchange reactions of bis(triethylgermyl) mercury with organotin halides and related compounds (42) have been investigated. Various reactions are given in Chart 3

$$(Me_3Si)_2Hg + R_3GeOMe \longrightarrow Me_3SiHgGeR_3 + (Me_3Ge)_2Hg$$

(R = Me, Et)

$$\begin{array}{lll} (Et_3Ge)_2Hg + Et_3SnX \xrightarrow[\text{10hr.}]{100^{\circ}} & Et_3GeHg\,X + & Et_3GeSnEt_3 \\ & \quad\downarrow & \quad(64.3\%) \\ & Et_3GeX + Hg & \\ & (90\%) \quad (94\%) & \end{array}$$

(X = Cl, OCOMe, NCO, NEt_2)

$$2(Et_3Ge)_2Hg + Et_2SnX_2 \longrightarrow 2Et_3GeX + (Et_3Ge)_2SnEt_2 + 2Hg$$

(X = Cl, OMe)

$$\begin{array}{llll} (Et_3Ge)_2Hg + Ph_3SnCl \xrightarrow[\text{12hr.}]{\text{PhMe; }100^{\circ}} & Et_3GeCl + & (Et_3Ge)_2 + & Ph_3SnGeEt_3 \\ & (85.6\%) & (9.9\%) & (41.5\%) \\ & + (Ph_3Sn)_2 + & Hg & \\ & (56.5\%) & (95.5\%) & \end{array}$$

Chart 3. Reactions of silyl- and germyl-mercury derivatives.

Vyazankin et al. extended their studies on the reactions of silyl- and germyl-mercury compounds with chalcogens and observed the formation of chalcogen-insertion products (43):

$$\begin{tikzcd}
(R_3M)_2Hg + \frac{1}{8}X_8 \arrow[r, "0 - 20^o", "pentane"'] & R_3MXHgMR_3 \arrow[d, "4hr."', "hv"] \\
& R_3MXMR_3 + Hg
\end{tikzcd}$$

(R = Et, i - Pr; M = Si, Ge; X = S, Se; yield:- 46 - 91%)

$$Et_3MHgEt + \frac{1}{8}X_8 \longrightarrow Et_3MXHgEt$$

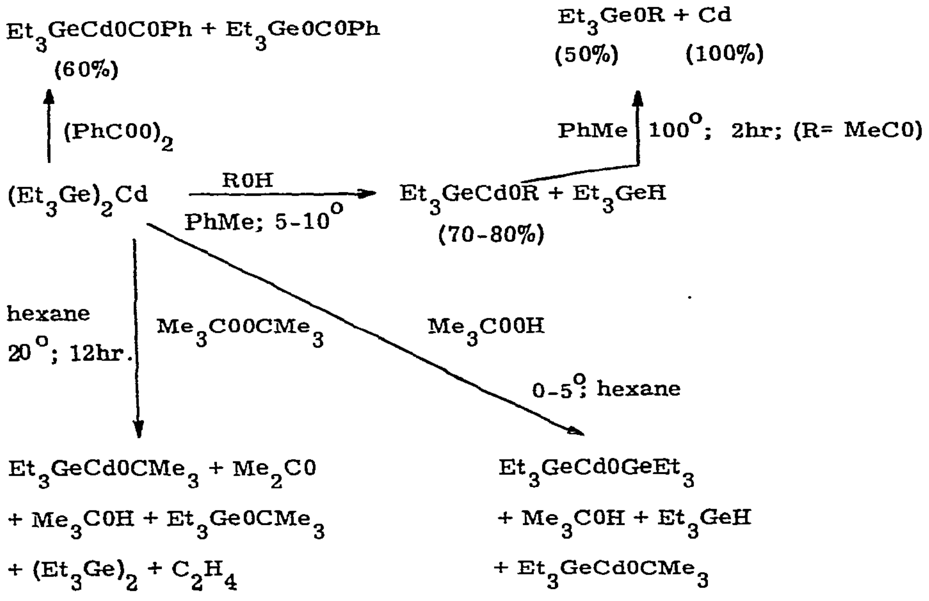
(M = Si, Ge; X = S, Se; yield:- 85 - 98%)

In view of the well-known susceptibility of organozinc and organocadmium compounds towards electrophilic attack, the hydrogermolysis of zinc-carbon or cadmium - carbon bonds seemed to be an appropriate possibility and indeed reaction of the type given below was found to occur giving zinc-germanium or cadmium-germanium bonded compounds (44):

$$2Ph_3GeH + R_2M.L \xrightarrow{80-130^o} (Ph_3Ge)_2M.L + 2RH$$

(R = Et, M = Zn; R = Me, M = Cd; L = TMED, Bipy, THF etc;
yield:- 35 - 80%)

The reactions of bis(triethylgermyl)cadmium with organic acids and peroxides etc. have been shown to proceed through the selective cleavage of the Ge-Cd-Ge linkage (45, 46). Some of these reactions are compiled in Chart 4.



(R = MeCO, PhCO, Ph)

Chart 4. Some reactions of bis(triethylgermyl)cadmium

The product composition in the reaction between triethylgermyllithium and trityl chloride has been attributed to the occurrence of an unusual bimolecular condensation complicated by halogen - metal exchange (47):

$$Et_3GeLi + Ph_3CCl \longrightarrow \left[\begin{matrix} Li^+ & GeEt_3 \\ Cl^- & CPh_3 \end{matrix}\right]$$

$$\downarrow$$

$$LiCl + Et_3Ge^{\cdot} + Ph_3C^{\cdot}$$

$$2Et_3Ge \rightleftharpoons Et_3GeGeEt_3$$

$$2Ph_3C^{\cdot} \rightleftharpoons Ph_3CCPh_3$$

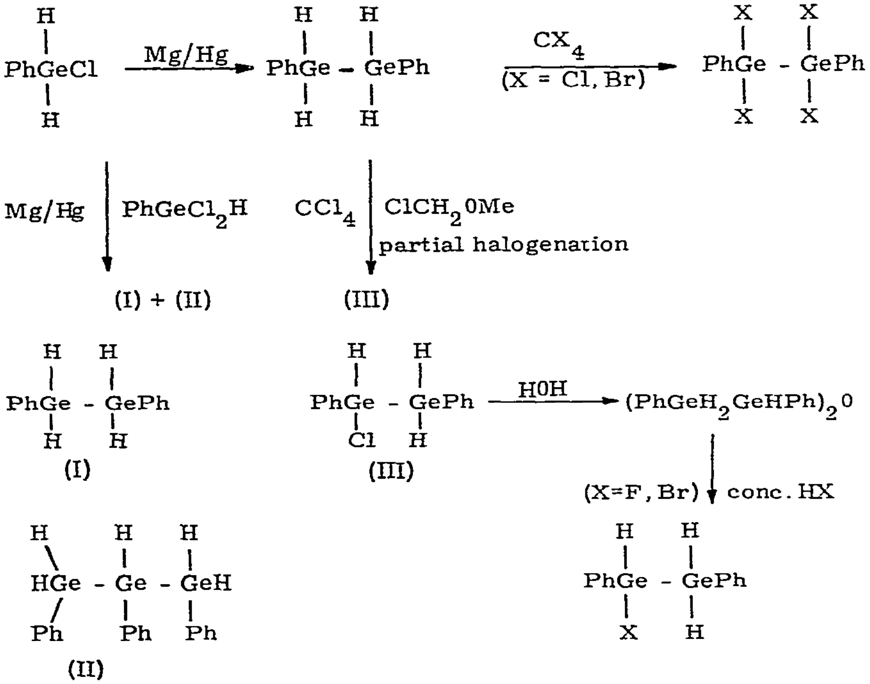
$$Et_3Ge^{\cdot} + Ph_3C^{\cdot} \rightleftharpoons Et_3GeCPh_3$$

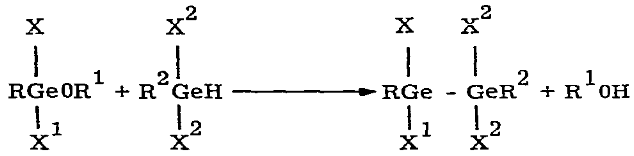
The reaction mechanism seems to be the one involving the one-electron transfer from triethylgermyllithium (the electron donor) to trityl chloride.

Bulten and Noltes investigated the effects of solvent, temperature, mode of addition, nature of the alkali metal, nature of the halogen and nature of the organic groups in the reaction of the type (48):

$$Et_3GeK + Me_3GeCl \xrightarrow[-60^{o}]{HMPT} Me_3GeGeEt_3 + KCl.$$

The partial halogenation of organohydrodigermanes (49), coupling reactions of organohydrohalogermanes (50) and hydrogermolysis of alkoxygermanes (51) have been used to synthesize a variety of di- and polygermanes (see Chart 5).





(85%)

(R = Ph, Cl, Br, 0Me ; X and X^1 = Cl, Br, 0Me Ph ; R^1 = Me, Ph, C_6H_{11} ; R^2 = Ph, Cl; X^2 = Cl, Br)

Chart 5. Synthesis of some di- and polygermanes.

A number of organosilyl - and organogermyl-substituted ferrocenes, which contain the M - M (M = Si, Ge) groupings have been prepared and some of their reactions studied (52 - 54). Various reactions are listed in Chart 6.

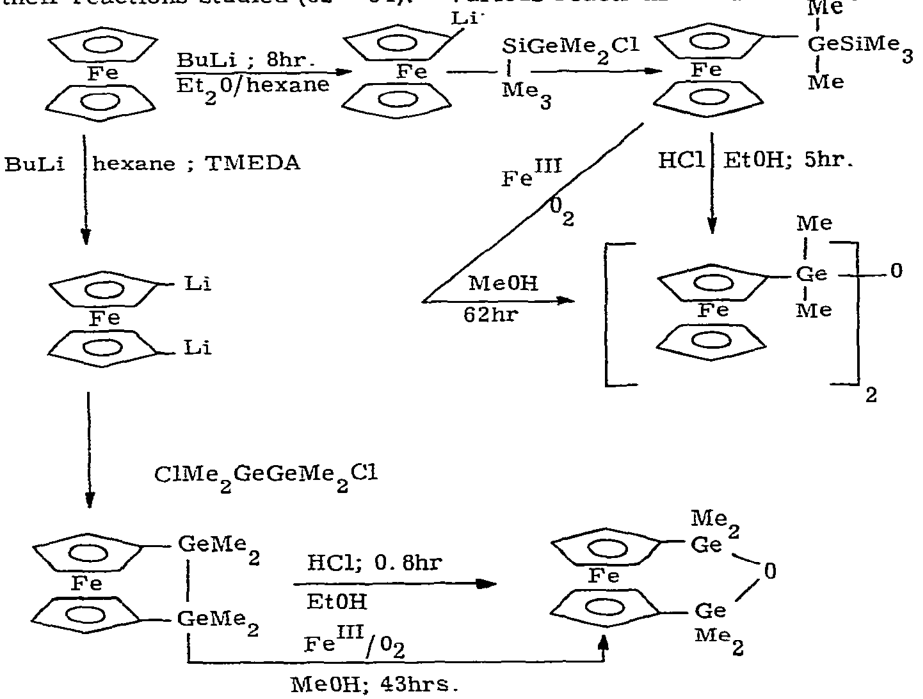
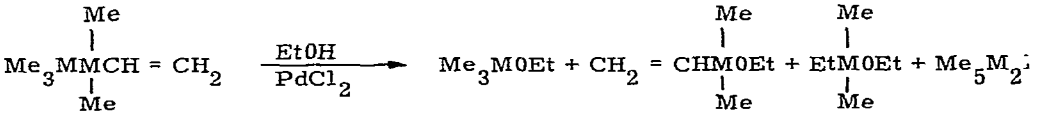


Chart 6. Synthesis and reactions of germyl-substituted ferrocenes.

Yamamoto and Kumada observed the cleavage of the germanium-germanium bond of vinylpentamethyldigermane by ethanol in the presence of palladium (II) chloride as catalyst at room temperature to give products analogous to those from the similar cleavage of vinylpentamethylsilane at 0°(55):



$$Me_3M\underset{\displaystyle Me}{\overset{\displaystyle Me}{M}}CH = CH_2 \xrightarrow[PdCl_2]{EtOH} Me_3MOEt + CH_2 = CH\underset{\displaystyle Me}{\overset{\displaystyle Me}{M}}OEt + Et\underset{\displaystyle Me}{\overset{\displaystyle Me}{M}}OEt + Me_5M_2$$

(M = Si, Ge)

The interesting feature of the reaction was that when an equimolar mixture of silicon and germanium derivative was treated with two equivalents of ethanol in the presence of palladium (II) chloride at room temperature, the germanium derivative reacted faster than the silicon compound. This difference of reactivity in separate ethanolysis experients and in a competitive experiment has been explained by assuming that (i) the vinyl derivative of digermane is more strongly complexed to the palladium catalyst than the silicon derivative, and (ii) nucleophilic attack of ethanol on the silicon is faster than on the germanium atom.

The germanium-germanium bond of hexaorganodigermanes could also be cleaved by reagents like ammonium hexachloroplumbate (56) and 1,2-dibromoethane (57) to give triorganohalogermanes:

$$Ph_3MMPh_3 + (NH_4)_2PbCl_6 \xrightarrow[30^o]{PhH} 2Ph_3MCl + 2NH_4Cl . + PbCl_2$$

(M = Ge, Sn, Pb)

$$Me_3GeGeMe_3 + BrCH_2CH_2Br \xrightarrow{(Ph\ COO)_2} 2Me_3GeBr + H_2C = CH_2$$

In the reaction with ammonium hexachloroplumbate, the order of reactivity has been shown to be as: Pb > Sn > Ge.

Savory and Wallbridge extended their investigations on the small nido-carborane compounds containing a $B - MMe_3 - B$ (M = Si, Ge) three-centre bond and observed that only the germanium derivative, $Me_3GeC_2Me_2B_4H_5$ isomerises to the terminal isomer (58). These compounds have been synthesized via the reaction:

$$Me_3MX + M^1C_2Me_2B_4H_5 \xrightarrow{Et_2O} Me_3MC_2Me_2B_4H_5$$

(X = Cl, Br; M^1 = Na, Li; M = Si, Ge; yield:- 60 - 80%)

The preparation and chemistry of μ-silyl and μ-germyl carboranes has been investigated in detail. These derivatives have been prepared according to the reaction (59):

$$\begin{tikzcd}
C_2B_4H_8 + NaH \arrow[r, "THF"] & Na^+ C_2B_4H_7^- + H_2 \arrow[d, "R_3MCl", "0^o"'] \\
 & \mu - R_3MC_2B_4H_7 + NaCl
\end{tikzcd}$$

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

These derivatives are stable at room temperature but are hydrolyzed by traces of moisture forming parent $C_2B_4H_8$. These species undergo rapid, essentially quantitative conversion to the respective 4-substituted (i.e. bridge-to-terminal rearrangement) derivatives at temperatures ranging from 80 - 175^o. The structure of these species has been proposed on the basis of their spectral data (see Fig. 1).

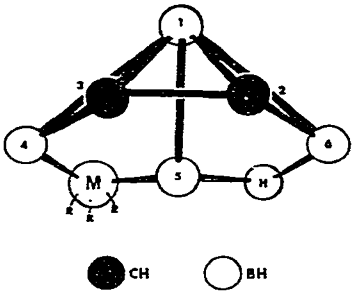


Fig. 1. Proposed structure of $\mu - R_3MC_2B_4H_7$ species (M=Si, Ge; R = H, Me) [from M.L. Thompson and R.N Grimes; Inorg. Chem. 11(1972)1925]

Norman and Loffredo claim to have synthesized the first germa- and stanna undecaborane derivatives via the reaction (60):

$$B_{10}H_{14} + NaH \longrightarrow NaB_{10}H_{13} \xrightarrow[Et_2O]{Me_3MX} Me_2MB_{10}H_{12} + NaX$$

(M = Ge, Sn; X = Br, Cl; yield:- 5 - 18%)

Proposed structure of these derivatives is given in Fig. 2 (derived from ^{11}B - NMR data).

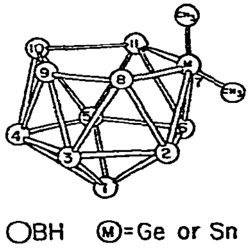
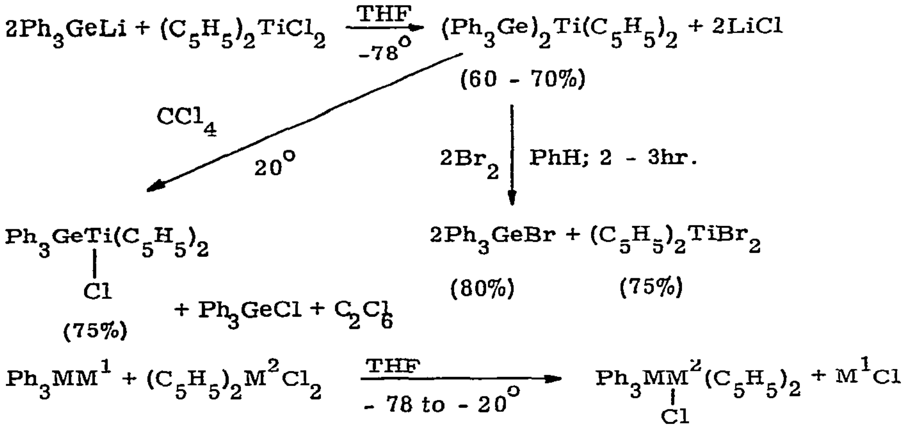


Fig. 2. A possible structure for $Me_2MB_{10}H_{12}$ (M = Ge, Sn) [from R.E. Loffredo and A.D. Norman; J.Amer.Chem.Soc. 93(1971)5587]

Various preparative routes, properties and reactions for the transition metal - Group IVB compounds have been reviewed (61 - 63). The compounds containing germanium - titanium (64), germanium - zirconium and germanium - hafnium (65) bonds, with the transition metal in a high (+ 4) oxidation state, have been synthesized according to the reactions given in Chart 7.



$$2Ph_3GeLi + (C_5H_5)_2TiCl_2 \xrightarrow[-78^o]{THF} (Ph_3Ge)_2Ti(C_5H_5)_2 + 2LiCl \quad (60 - 70\%)$$

$$(Ph_3Ge)_2Ti(C_5H_5)_2 \xrightarrow[20^o]{CCl_4} Ph_3GeTi(C_5H_5)_2Cl \ (75\%) + Ph_3GeCl + C_2Cl_6$$

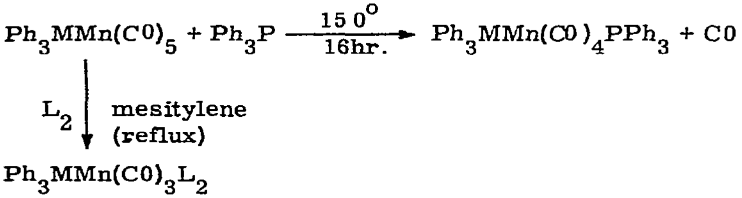
$$(Ph_3Ge)_2Ti(C_5H_5)_2 \xrightarrow[PhH;\ 2 - 3hr.]{2Br_2} 2Ph_3GeBr \ (80\%) + (C_5H_5)_2TiBr_2 \ (75\%)$$

$$Ph_3MM^1 + (C_5H_5)_2M^2Cl_2 \xrightarrow[-78 \text{ to } -20^o]{THF} Ph_3MM^2(Cl)(C_5H_5)_2 + M^1Cl$$

(M = Si, Ge, Sn; M^1 = Li, Na; M^2 = Zr, Hf)

Chart 7. Synthesis of some Ge - Ti, Ge - Zr and Ge - Hf compounds.

Ross and coworkers observed the reactions of $Ph_3MMn(CO)_5$ (M = Si, Ge, Sn) complexes with Lewis bases to result in displacement of carbon monoxide (66):

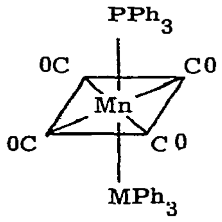


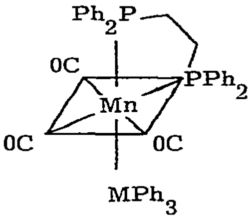
$$Ph_3MMn(CO)_5 + Ph_3P \xrightarrow[16hr.]{150^o} Ph_3MMn(CO)_4PPh_3 + CO$$

$$Ph_3MMn(CO)_5 \xrightarrow[\text{mesitylene (reflux)}]{L_2} Ph_3MMn(CO)_3L_2$$

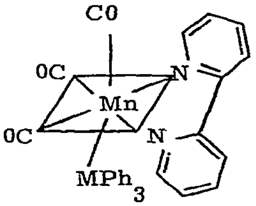
(L_2 = dipy, diphos; M = Si, Ge, Sn)

The carbonyl stretching spectra for the products indicate that for triphenylphosphine and diphos the trans isomers,





are obtained, while for dipy the cis isomers,



are formed.

The reactions of $Me_3MMn(CO)_5$ (M = Si, Ge) with unsaturated fluorocarbons (e.g. perfluorocyclobutene, perfluoro-2-butyne or 3,3,3-trifluoropropyne) have been shown to give either products of insertion into the M - Mn bond, or compounds formed by the decomposition of such insertion products (67). Germylpentacarbonylmanganese could be synthesized in upto 86% yield according to the reaction (68):

$$H_3GeBr + NaMn(CO)_5 \xrightarrow[THF]{Et_2O\ or} H_3GeMn(CO)_5 + NaBr$$

The product has been shown to be considerably more stable both thermally and chemically than the analogous cobalt complex $[H_3GeCo(CO)_4]$. The chemistry of Re - M (M = Ge, Sn) derivatives has been reviewed (69).

Organometallic compounds containing germanium - iron bond have been prepared by a variety of methods (70 - 73). Some of these are compiled in Chart 8.

$$\left[(C_5H_5)M(CO)_n\right]_2 + GeX_4 \xrightarrow{PhH} (C_5H_5)M(CO)_nGeX_3 + (C_5H_5)M(CO)_nX$$

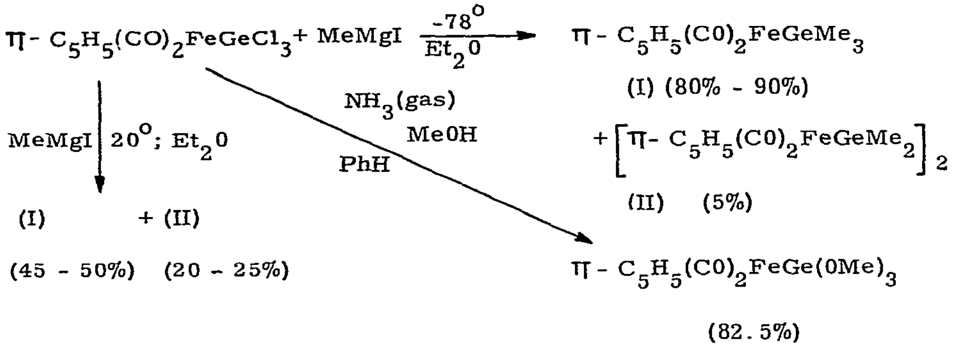
$$\begin{bmatrix} M = Fe;\ n = 2;\ X = Cl,\ Br,\ I \\ M = Ni;\ n = 1;\ X = Cl,\ Br,\ I \end{bmatrix}$$

$$\left[\pi\text{-}C_5H_5Fe(CO)_2\right]_2 Hg + GeI_2 \xrightarrow[6hr.]{PhH:80^o} \left[\pi\text{-}C_5H_5Fe(CO)_2\right]_2 GeI_2 + Hg$$

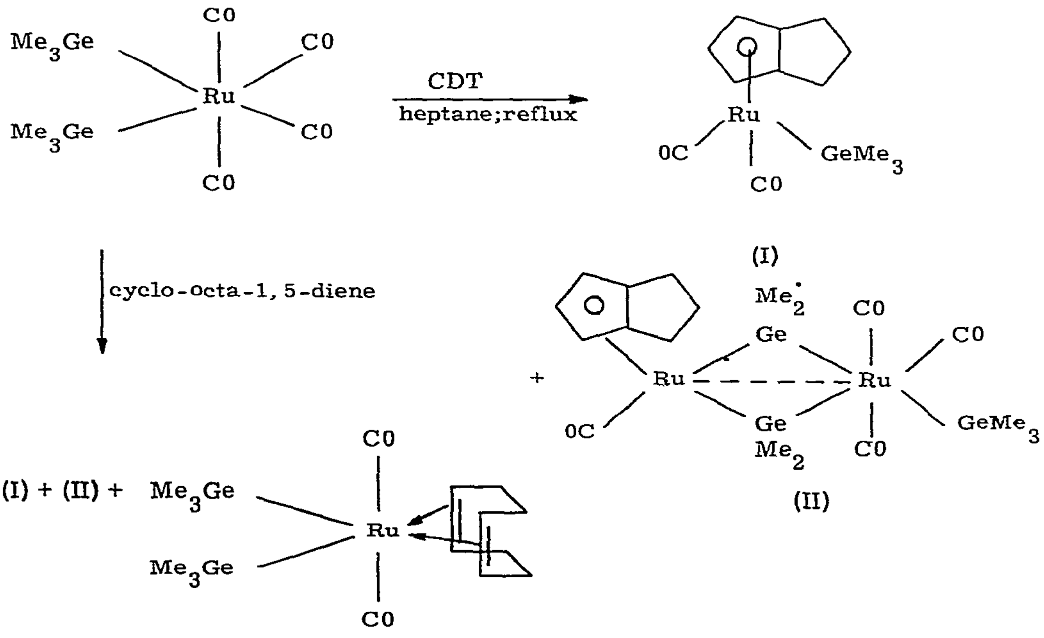
$$H_3GeCl + Na_2Fe(CO)_4 \xrightarrow[0^o]{n\text{-}butane} (H_3Ge)_2Fe(CO)_4 + H_3Ge(H)Fe(CO)_4$$

Cnart 8. Synthesis of some Ge - Fe derivatives.

Nesmeyanov and coworkers achieved the alkylation and alkoxylation at the germanium atom, of the compound: π- $C_5H_5(CO)_2FeGeCl_3$, without rupture of the iron - germanium bond (74):



Ring contraction of trans, trans , trans-cyclododeca - 1, 5, 9 - triene (CDT) has been accomplished by its reaction with bis(trimethylgermyl)tetracrabonyl-ruthenium (75):



Mackay et al. reported the synthesis of germyltetracarbonylcobalt according to the reaction (76):

$$H_3GeBr + NaCo(CO)_4 \xrightarrow{Et_2O} \underset{(48\%)}{H_3GeCo(CO)_4} + NaBr$$

The germanium - cobalt bond of the compound could be cleaved by dry HCl, $HgCl_2$ and air:

$$\begin{tikzcd}
H_3GeCo(CO)_4 \arrow[r, "HCl"] \arrow[d, "HgCl_2"] & H_3GeCl + GeH_4 \\
H_3GeCl + Hg\left[Co(CO)_4\right]_2 + ClHgCo(CO)_4 &
\end{tikzcd}$$

In general, $H_3GeCo(CO)_4$ reacts with nitrogen - containing bases to form solid, involatile, white to brown approximately 1 : 2 adducts, $H_3GeCo.(CO)_4.2B$ Only with the very strong base piperidine is a relatively stable compound obtained; an order of stability B = piperidine > triethylamine ≈ trimethylamine >> pyridine is indicated .

The reactions of trans- $(Ph_3P)_2(CO)ClIr$ with compounds of the type R_3MH(R = Cl, Me, Bu; M = Si, Ge, Sn) have been shown to give the dihydridoiridium complexes of the type $(Ph_3P)_2(R_3M)(CO)(H_2)Ir$(I) (77) The exchange reactions between (I) (R = Me_3Ge) and silanes and stannanes favour reaction products in the order: $Cl_3Si > Bu_3Sn \sim Me_3Sn > Me_3Ge > Me_3Si$ and $Cl_3Ge > Me_3Ge$.

Eaborn and coworkers reported the preparation of the first compound with an optically - active silicon or germanium atom bonded to platinum (78):

$$\begin{tikzcd}
Et(1\text{-}C_{10}H_7)PhGeH + trans\text{-}\left[PtHCl(PMe_2Ph)_2\right] \arrow[d, "70^\circ"', "8hr."] \\
trans\text{-}\left\{PtCl\left[GeEt(C_{10}H_7)Ph\right](PMe_2Ph)_2\right\} + H_2
\end{tikzcd}$$

The thermally induced interaction of trichlorogermane with potassium tetrachloroplatinate in methanol saturated with hydrogen chloride has been shown to give a new metal atom cluster compound $\left[Pt(GeCl)(GeCl_3)\right]_4$ (79).

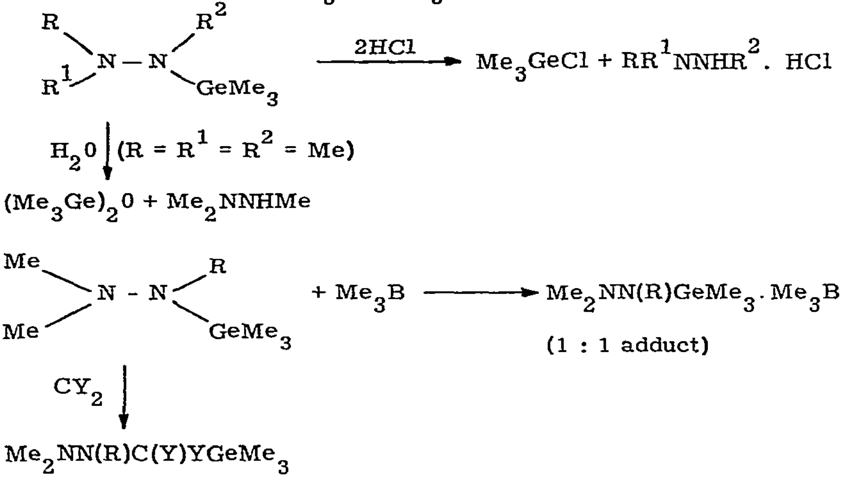
Germanium - nitrogen compounds

Peterson and Thé synthesized a number of substituted germylhydrazines and studied some of their reactions (80 - 82). Some of their results are summarized in Chart 9.

$$Me_3GeX + (RR^1R^2N_2)Li \longrightarrow Me_3GeN_2RR^1R^2 + LiX$$

$$Me_2GeX_2 + 2(RR^1R^2N_2)Li \longrightarrow Me_2Ge(N_2RR^1R^2)_2 + 2LiX$$

$(R, R^1, R^2 = H, Me, SiMe_3, GeMe_3; X = Cl, Br)$

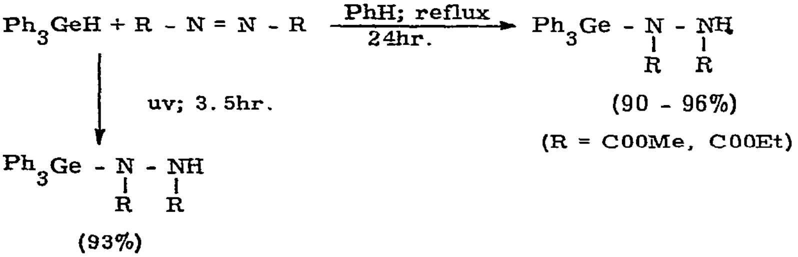


$(R = H, Me, SiMe_3; Y = O, S)$

Chart 9. Synthesis and reactions of germylhydrazines.

On the basis of PMR spectra, the metalloid - substituted nitrogen atom rathe than the terminal nitrogen, is indicated as the base centre at which adduct formation occurs (81).

Another synthetic route to germyl-hydrazines involves the reaction (83):



$$Ph_3GeH + R - N = N - R \xrightarrow[24hr.]{PhH;\ reflux} Ph_3Ge - N(R) - NH(R)$$

(90 - 96%)

(R = COOMe, COOEt)

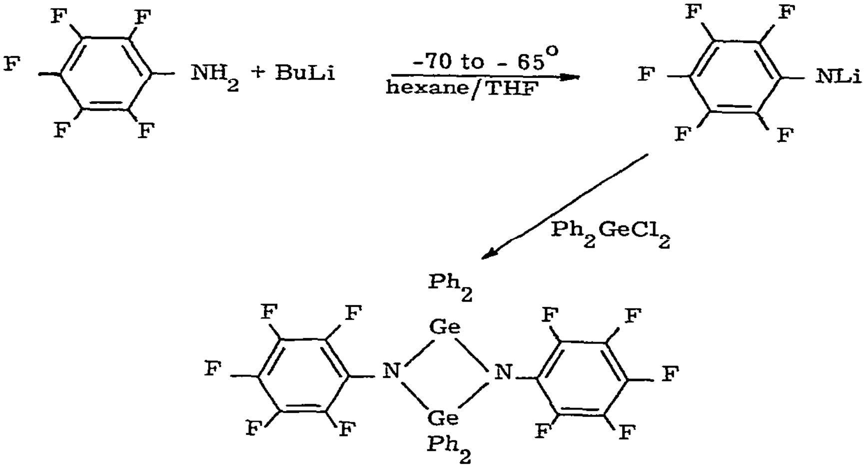
$$Ph_3GeH + R - N = N - R \xrightarrow{uv;\ 3.5hr.} Ph_3Ge - N(R) - NH(R)$$

(93%)

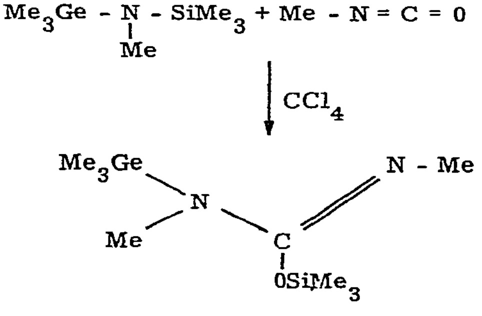
(R = COOEt)

References p. 276

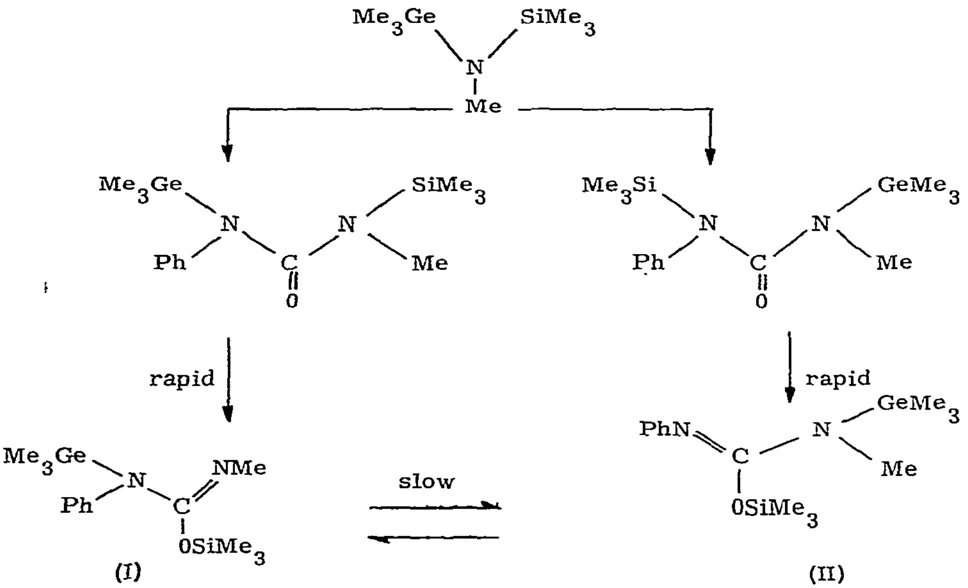
The preparation of N - perfluorophenyl substituted cyclodigermazane has been reported (84):



The addition reactions of heptamethylsilagermazane with isocyanates or isothiocyanates have been elucidated spectroscopically (85). The substituents on the heterocumulenes, the migratory aptitudes of the Me_3M groups ($Me_3Si > Me_3Ge > Me_3Sn$) and the affinity of each metal for the nitrogen, oxygen or sulfur atom determines which of the possible isomeric structures is favoured in each case. Thus the addition reaction of heptamethylsilagermazane with methyl isocyanate took place exothermally giving the adduct whose structure was confirmed by IR and NMR spectroscopy:

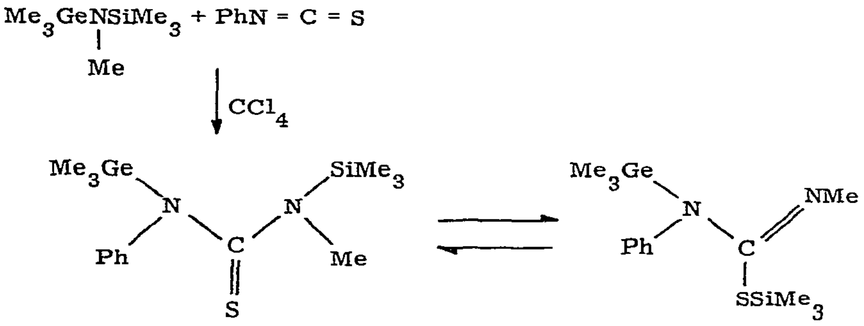


When phenyl isocyanate was used as an acceptor molecule, somewhat more complicated behaviour was observed. Using NMR spectroscopy, various observations have been explained in terms of the following scheme:

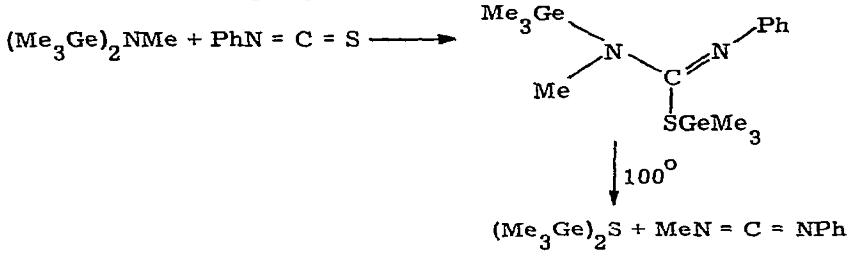


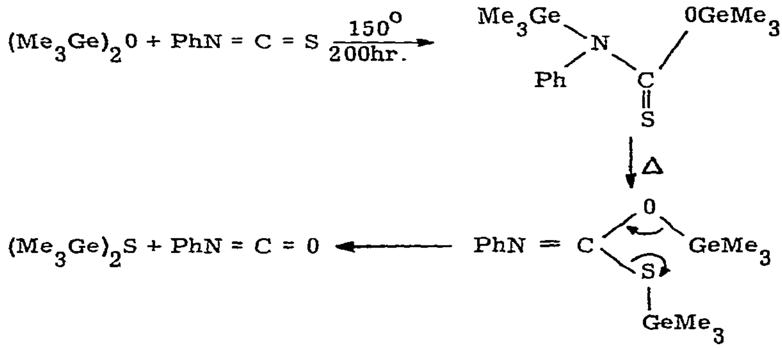
$\left[\ (I)/(II) = 1/2.5\ \right]$

Finally the reaction with phenyl isothiocyanate has been shown to proceed as:



Further investigations have shown that the addition - elimination reactions of heptamethyldigermazane or hexamethyldigermoxane with phenyl isothiocyanate lead to the selective formation of $(Me_3Ge)_2S$, a behaviour quite similar to that of the corresponding organotin analogues (86):



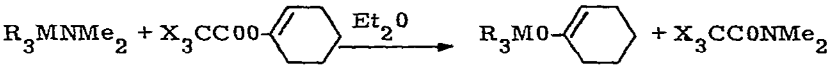


The reactions of (trialkylgermyl) dialkylamines with cyclic ethers have been shown to give germyloxyalkylamines (87):

$$Et_3GeNR_2 + (CH_2)_nO \xrightarrow{ZnCl_2} Et_3GeO(CH_2)_nNR_2$$

[R = Me; n = 2, 3, 4; yield:- 49 - 100%
R = C_6H_{11}; n = 2; yield:- 60 - 80%]

Lutsenko et al. observed that trialkyl (dimethylamino) - silanes and -germanes react vigorously with 1 - cyclohexen - 1- yl trihaloacetates to give 1 - cyclohexen - 1 - yloxy derviatives of silicon and germanium in yields of about 80% (88):



(M = Si, Ge; R = Me, Et; X = F, Cl)

The application in organometallic synthesis of some acyl - bond cleavage reactions by (triethylgermyl) dimethylamine has been studied (89). Some of the reactions are listed in Chart 10.

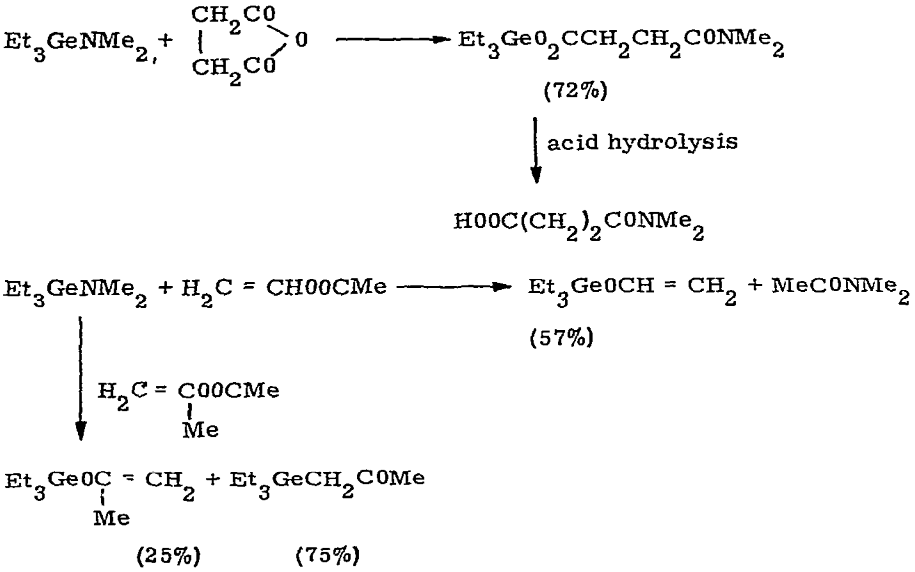
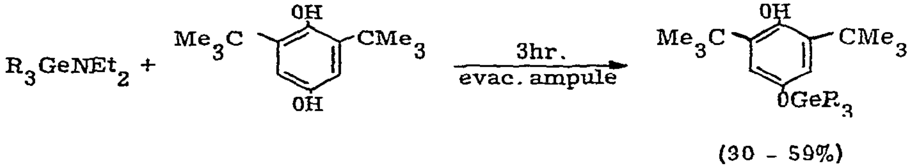
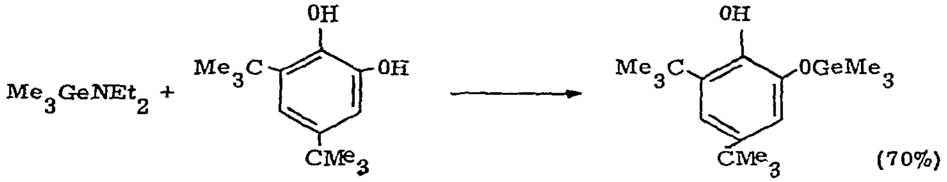


Chart 10. Some reactions of (triethylgermyl) dimethylamine.

Phenols containing heteroorganic groups as substituents have been synthesize using aminogermanes as the germylating agents (90):



(R = Me, Et)

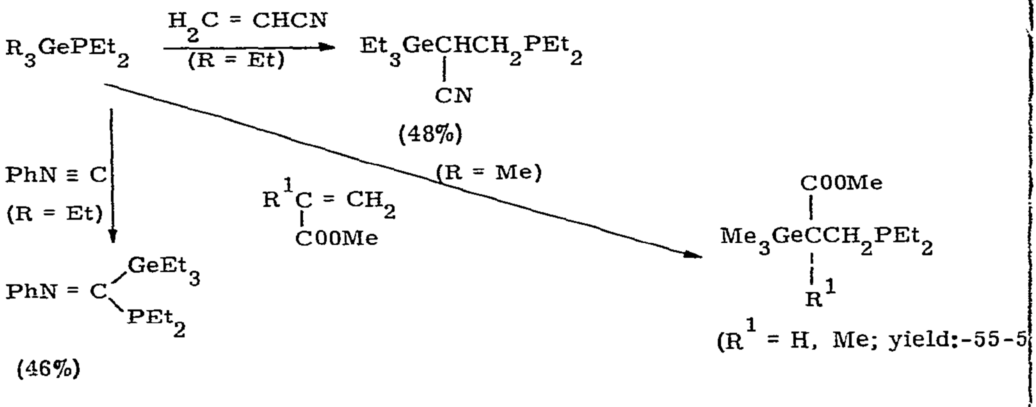


Abel and coworkers synthesized a good range of ketenimino-derivatives of silicon, germanium, tin and boron via the 1,4-insertion reactions of 1,1-bis-(perhalomethyl)-2,2-dicyanoethylenes (91):

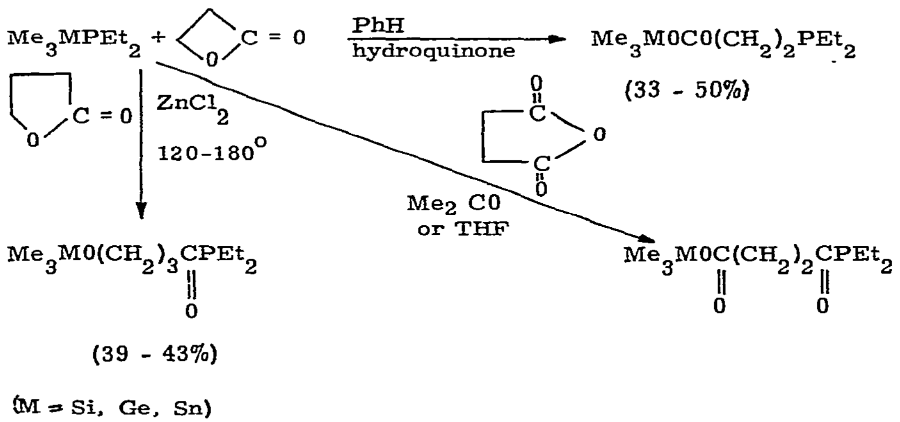
$$n\text{-}Bu_3GeNMe_2 + (CF_3)_2C = C(CN)_2 \longrightarrow n\text{-}Bu_3GeN{=}C{=}C(CN)C(CF_3)_2NMe_2$$

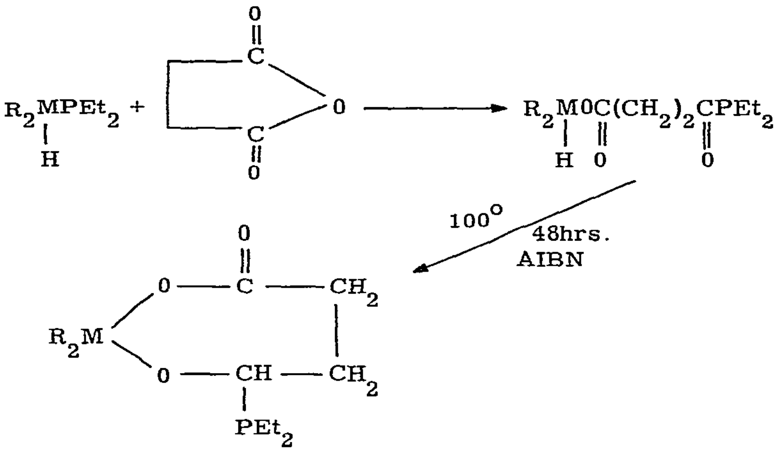
Germanium - phosphorus and - arsenic compounds

The addition of germylphosphines to several ethylenic compounds has been reported to proceed via a nucleophilic attack of phosphorus at the double bond (92):



Satgé et al. investigated the reactions of oxygen containing heterocycles with trialkyl - silyl - , - germyl - and stannyl - phosphines (93, 94). Some of their results are compiled in Chart 11.

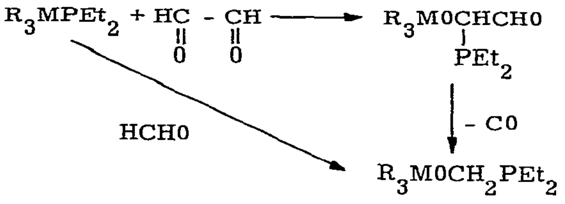




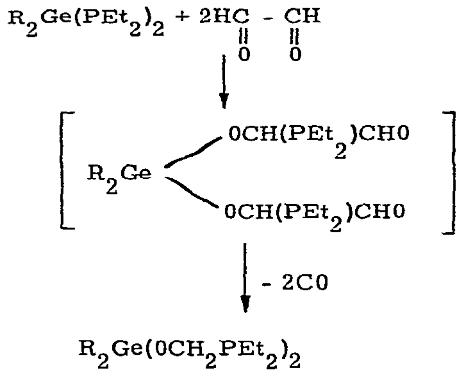
(R = Me, Et; M = Si, Ge; AIBN = azobisisobutyronitrile
yield:- 81% for R = Et, M = Ge)

Chart 11. Some reactions of trialkyl germylphosphines and related compounds.

The germyl - and silyl - phosphines have been shown to add readily to o of the carbonyl groups of glyoxal. The phosphorized germoxy or siloxy aldehydes thus formed are unstable and decarbonylate readily (95):



(R = Me; M = Si, Ge)



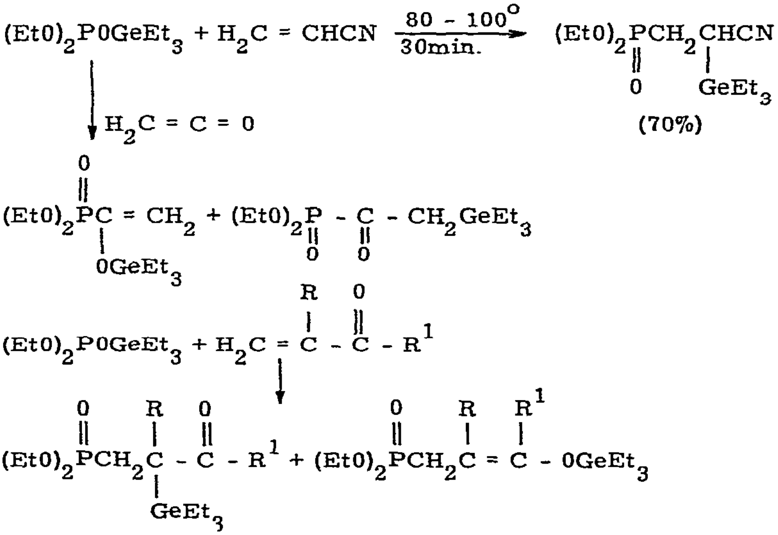
$$R_2Ge(PEt_2)_2 + 2HC(=O)-CH(=O) \longrightarrow \left[R_2Ge\begin{matrix} OCH(PEt_2)CHO \\ OCH(PEt_2)CHO \end{matrix} \right] \xrightarrow{-2CO} R_2Ge(OCH_2PEt_2)_2$$

(R = Me, Et)

Lutsenko and coworkers synthesized some trialkylgermyl dialkylphosphites (96) and studied their reactions with a variety of unsaturated compounds. Various reactions are given in Chart 12.

$$R^1{}_3GeCl + NaOP(OR)_2 \xrightarrow{Et_2O} R^1{}_3GeOP(OR)_2 + NaCl \quad (40 - 50\%)$$

(R = Et; R^1 = Me, Et)



$$(EtO)_2POGeEt_3 + H_2C=CHCN \xrightarrow[30min.]{80 - 100^\circ} (EtO)_2P(=O)CH_2CH(GeEt_3)CN \quad (70\%)$$

$$(EtO)_2POGeEt_3 \xrightarrow{H_2C=C=O} (EtO)_2P(=O)C(OGeEt_3)=CH_2 + (EtO)_2P(=O)-C(=O)-CH_2GeEt_3$$

$$(EtO)_2POGeEt_3 + H_2C=C(R)-C(=O)-R^1 \longrightarrow (EtO)_2P(=O)CH_2C(R)(GeEt_3)-C(=O)-R^1 + (EtO)_2P(=O)CH_2C(R)=C(R^1)-OGeEt_3$$

(R = H, R^1 = H; R = Me, R^1 = OMe)

Chart 12. Synthesis and reactions of some trialkylgermyl dialkylphosphites.

An efficient method of synthesizing phosphino-Group IVB compounds has been reported (97):

$$4H_3GeBr + LiAl(PH_2)_4 \xrightarrow[\text{ether}]{-45^{\circ}} \underset{(87\%)}{4H_3GePH_2} + LiBr + AlBr_3$$

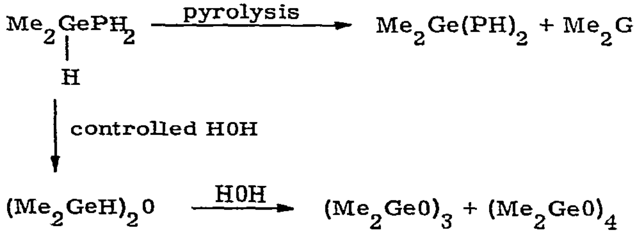
Schumann and Kuhlmey synthesized some organometal phosphine substituted transition metal complexes via the reaction (98):

$$2(Me_3M^1)_3P + M(CO)_6 \xrightarrow[h\nu]{60^{\circ}} (Me_3M^1)_2PM(CO)_4$$

$(M^1 = C, Ge, Sn;\ M = Cr, Mo. W)$

Some reactions of mono- and bis(phosphino) diorganogermanes have been the subject of a Ph.D. thesis (99):

$$6Me_2Ge(PH_2)_2 \xrightarrow[\text{condensation}]{\text{thermal}} (Me_2\ Ge)_6P_4 + 8PH_3$$



$$\begin{tikzcd}[column sep=large]
\underset{\displaystyle H}{Me_2GePH_2} \arrow[r, "\text{pyrolysis}"] \arrow[d, "\text{controlled HOH}"] & Me_2Ge(PH)_2 + Me_2GeH_2 \\
(Me_2GeH)_2O \arrow[r, "\text{HOH}"] & (Me_2GeO)_3 + (Me_2GeO)_4
\end{tikzcd}$$

Drake and Anderson accomplished the synthesis of some new germanium arsines and studied some of their reactions (100). Some of their results are given in Chart 13.

$$\begin{tikzcd}
4R_3GeBr + LiAl(AsMe_2)_3H \arrow[r, "-45^{\circ}"] & 3R_3GeAsMe_2 + R_3GeH + LiBr + AlBr_3 \\
Me_2AsH + LiAlH_4 \arrow[u, "Et_2O" ', "\text{diglyme}"] &
\end{tikzcd}$$

$(R = H, Me)$

$$Me_3GeNMe_2 + R_2AsH \xrightarrow{Et_2O} Me_3GeAsR_2 + Me_2NH$$

$(R = Me, Ph)$

$$Me_{4-n}Ge(AsMe_2)_n + 2nMeI \longrightarrow Me_{4-n}GeI_n + nMe_4AsI$$

(n = 1 - 3)

$$\begin{tikzcd} 3Me_3GeAsH_2 \arrow[r, "100^{o}", "24hr"'] & (Me_3Ge)_3As + 2AsH_3 \arrow[d, "HCl"] \\ & 3Me_3GeCl + AsH_3 \end{tikzcd}$$

Chart 13. Synthesis and reactions of some germanium arsines.

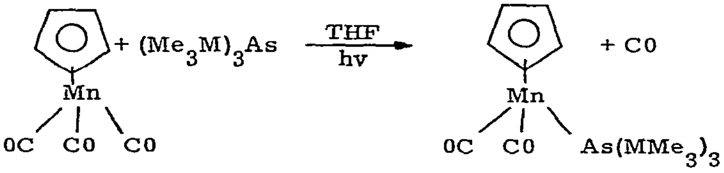
Organometal arsine substituted transition metal complexes have been synthesized via following reactions (101):

$$(Me_3M)_3As + M^1(CO)_6 \xrightarrow[hv]{THF} (Me_3M)_3AsM^1(CO)_5 + CO$$

(M = C, Si, Ge, Sn; M^1 = Cr, Mo, W; yield:- 31 - 94%)

$$(Me_3M)_3As + Fe(CO)_5 \xrightarrow[THF]{hv} (Me_3M)_3AsFe(CO)_4 + CO$$

(M = Ge, Sn; yield:- 40 - 80%)



(M = Ge, Sn; yield:- 85 - 92%)

Germanium - oxygen compounds

The metal alkoxides including those of germanium could be synthesized by electrolysis of anhydrous alcohols with a supporting electrolyte (e.g. quaternary ammonium salts) and a consumable anode of the metal (Ge, Ti, Zr · etc.) (102, 103).

The cleavage reactions of germanium-oxygen bond (104, 105), the reactions of cyanuryl chloride with germoxanes (106) and those of triethylmethoxygermane with pyran (107) have been reported . Some of these reactions are listed in Chart 14.

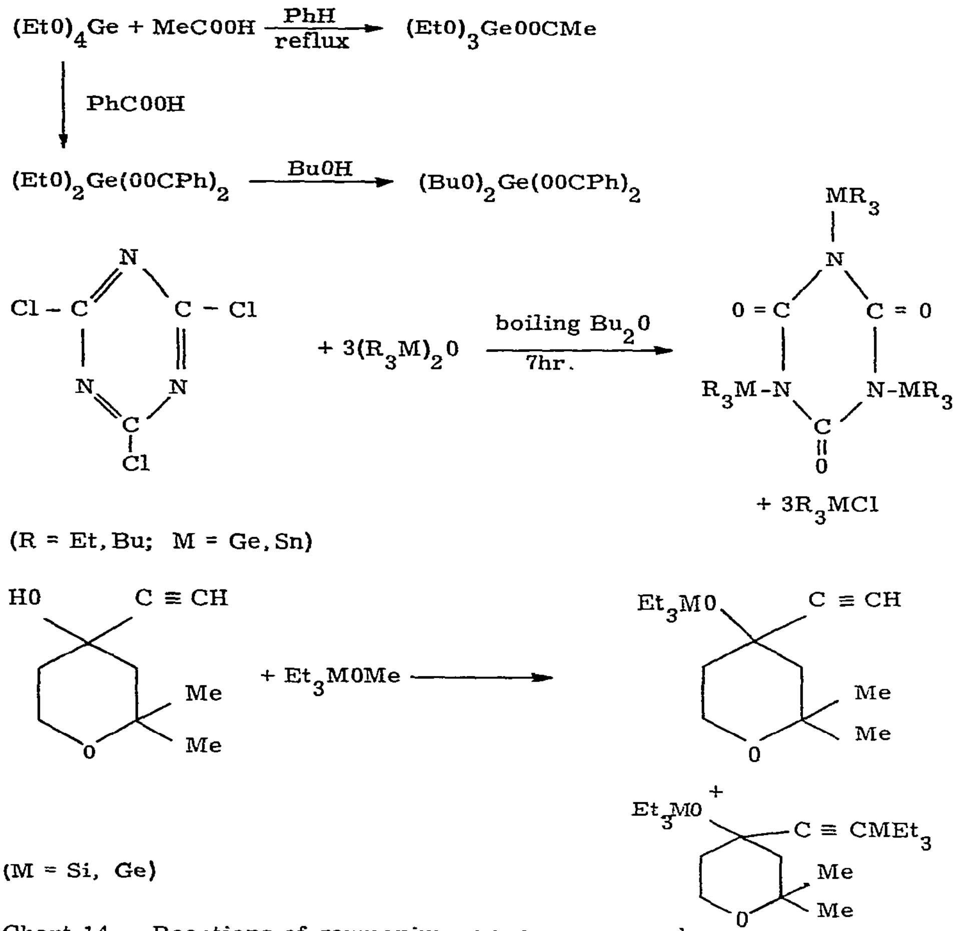


Chart 14. Reactions of germanium-oxygen compounds.

Lindner and Schardt synthesized some germanium sulfinates according t the reaction (108):

$$R_3GeBr + R^1SO_2Ag \xrightarrow[Me_2CO]{25^o} R_3GeO_2SR^1 + AgBr$$

(R = Et, Ph; R^1 = Ph, p - MeC_6H_4; yield:- 80 - 90%)

The spectral data of the compounds are indicative of sulfinic acid esters in which RSO_2^- residue is linked to the germanium via an oxygen atom.

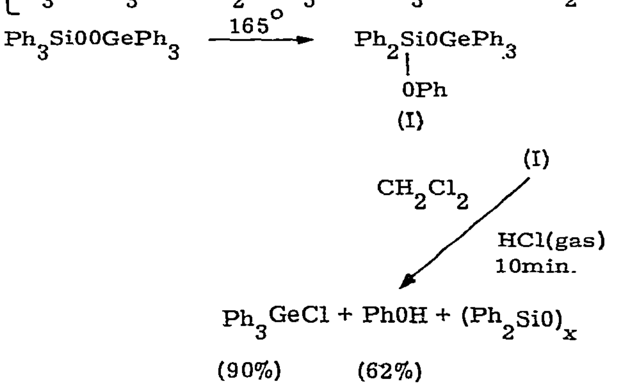
The preparative routes to various (109) peroxides (including organometallic peroxides) and the reactions of alkyl and acyl peroxides and hydroperoxides with organometallic compounds have been reviewed (110).

Catalytic decomposition of Ph_3MOOH (M = Ge, Sn) in sulfuric acid has been shown to give hydrogen peroxide and no rearrangement products. The germaniu derivative did not decompose in dioxane at ≤ 90° whereas Ph_3SnOOH did even at 10 - 40° (111).

Thermolysis of organometallic peroxides (including those of germanium) in heptane, anisole and cumene has been shown to proceed according to the reaction (112, 113):

$$Ph_3GeOOSiR_3 \longrightarrow Ph_3GeOSiR^1_3$$

[$R_3 = Me_3$, $PhMe_2$, Ph_3 and $R^1_3 = (OMe)Me_2$, $(OPh)Me_2$, $(OPh)Ph_2$ respectively.



$$Ph_3SiOOGePh_3 \xrightarrow{165^{\circ}} Ph_2Si(OPh)OGePh_3 \text{ (I)}$$

$$\text{(I)} \xrightarrow[\text{HCl(gas) 10min.}]{CH_2Cl_2} Ph_3GeCl + PhOH + (Ph_2SiO)_x$$

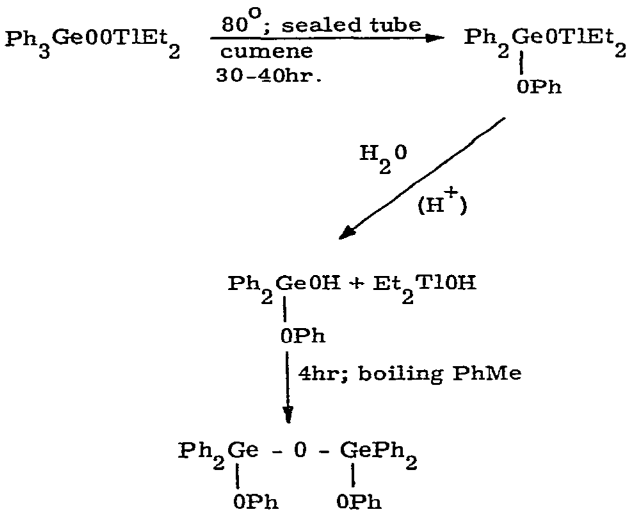
(90%) (62%)

The rate constants for the decomposition change linearly with increase in the number of phenyl groups in the peroxide (112).

Razuvaev and coworkers synthesized a bi-organometallic peroxide via the reaction (114):

$$Ph_3GeOOH + Et_3Tl \xrightarrow{PhH} Ph_3GeOOTlEt_2 + EtH.$$

Analogous silicon compound was found to rearrange rapidly whereas the germanium product rearranged only on heating:



$$Ph_3GeOOTlEt_2 \xrightarrow[\text{cumene; 30-40hr.}]{80^{\circ}\text{; sealed tube}} Ph_2\underset{OPh}{Ge}OTlEt_2 \xrightarrow[(H^+)]{H_2O} Ph_2\underset{OPh}{Ge}OH + Et_2TlOH \xrightarrow{\text{4hr; boiling PhMe}} Ph_2\underset{OPh}{Ge} - O - \underset{OPh}{Ge}Ph_2$$

Germanium - sulfur, - selenium and - tellurium compounds

The trimethylmetal (metal = Si, Ge, Sn) derivatives of thioglycol could be synthesized via following routes (115):

$$Me_3GeCl + HSCH_2CH_2OH \xrightarrow[Et_3N]{PhH} Me_3GeSCH_2CH_2OH \quad (70\%)$$

$$\xrightarrow{\text{heat}} HSCH_2CH_2OH + Me_3GeS(CH_2)_2OGeMe_3$$

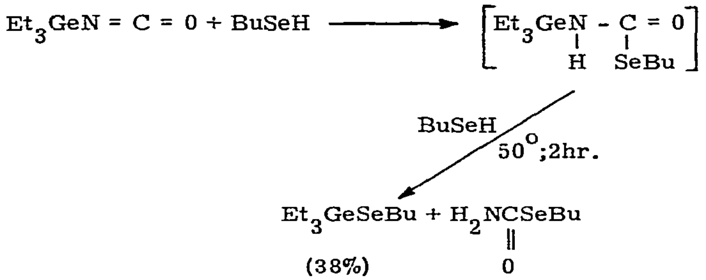
$$2Me_3GeCl + HS(CH_2)_2OH \xrightarrow[Et_3N]{PhH} Me_3GeS(CH_2)_2OGeMe_3$$

$$2Me_3GeS(CH_2)_2OH + (Me_3Si)_2NH \longrightarrow 2Me_3SiO(CH_2)_2SGeMe_3 + NH_3$$

The preparation of a number of compounds containing a Ge-Se bond has been accomplished according to the reactions (116 - 118):

$$R_3MNCNMR_3 + 2n - BuSeH \xrightarrow[100^{\circ}\text{; 1hr.}]{PhH} 2n - BuSeMR_3 + NH_2CN$$

(R = Me, Et, n - Bu, Ph; M = Si, Ge, Sn; yield:- 60 - 70%)



Some reactions of organometallic chalcogenides with mercury derivatives have been shown to proceed under mild conditions (119):

$$(Et_3M)_2E + HgX_2 \xrightarrow[50^o]{THF} 2\ Et_3MX + HgE$$

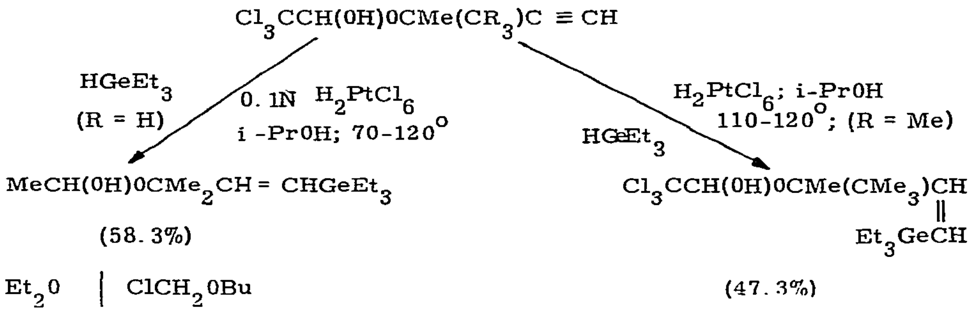
(M = Si, Ge; E = Se, Te; X = Cl, CN)

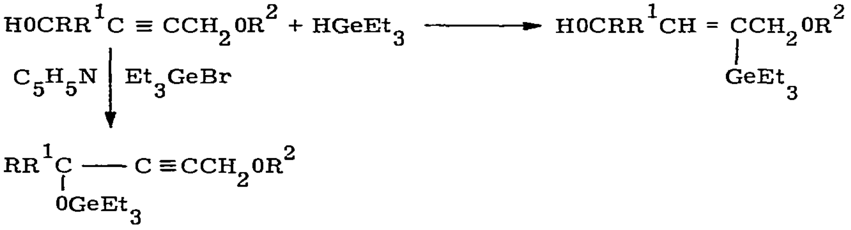
$$Et_3SiEH + (Et_3Ge)_2Hg \xrightarrow[-\ 20^o;\ 2\ -\ 3\ min.]{hexane} Et_3SiEHgGeEt_3 + Et_3GeH$$

(E = Se, Te)

Alkenyl - and alkynyl - germanium compounds

A number of publications regarding the addition of organohydrogermanes to alkynyl derivatives have appeared (120 - 124). The reactions provide convenie routes to alkenyl - germanium compounds. Some of the reactions are given in Chart 15.





$$HOCRR^1C \equiv CCH_2OR^2 + HGeEt_3 \longrightarrow HOCRR^1CH = C(GeEt_3)CH_2OR^2$$

$$HOCRR^1C \equiv CCH_2OR^2 \xrightarrow[C_5H_5N]{Et_3GeBr} RR^1C(OGeEt_3)-C \equiv CCH_2OR^2$$

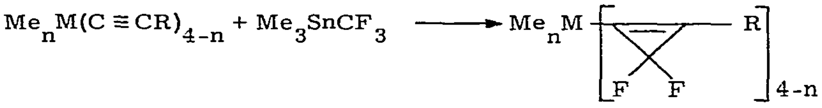
(R = Me, Et, Pr; R^1 = H Me; R^2 = Me Et)

$$F - C \equiv CH + Ph_3GeH \xrightarrow[31hr.]{120\text{-}130^o} F - CH = CHGePh_3$$

(F = ferrocenyl group)

Chart 15. Addition reactions of organohydrogermanes to alkynyl compounds.

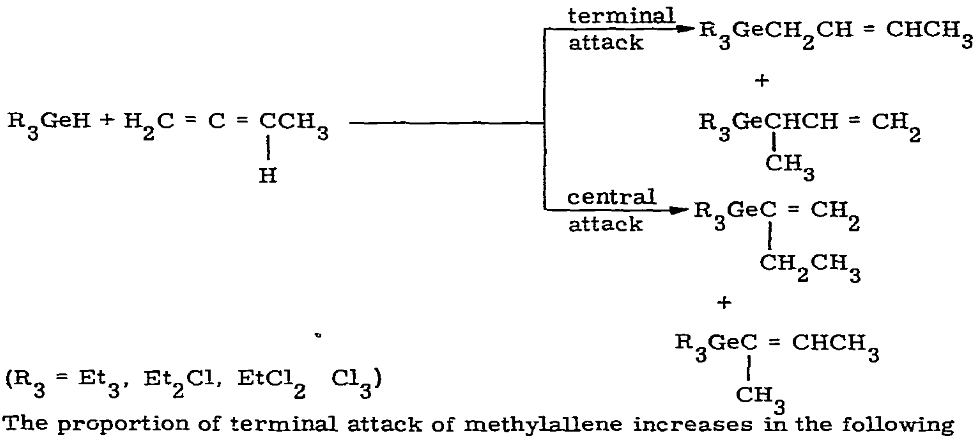
Cullen and Waldman extended their studies on the fluoroalkynyl derivatives of germanium and tin (see AS71, p. 154) and observed their reactions with Me_3SnCF_3 (125) to proceed as:



The reaction probably involves the addition of CF_2 to the carbon-carbon triple bond , and the carbene is probably produced in the singlet state by thermolysis of the tin compound.

The investigations on hydrogermylation of olefins (126) and acetylenes (127) in the presence of a catalyst have been reported. The relative amounts of the isomers depend on the catalyst, the organogermane, the ratio of reactant concentration and the catalyst concentration (127).

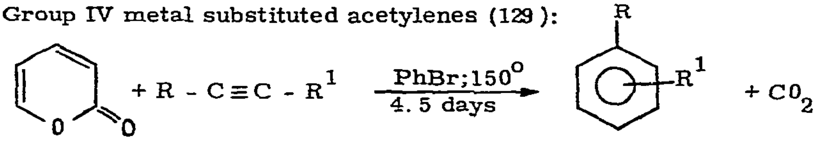
The addition of hydro- and halohydro-germanes to allenes in the presence of a catalyst (H_2PtCl_6, azobisisobutyronitrile) has been shown to proceed according to the scheme (128):



(R_3 = Et_3, Et_2Cl, $EtCl_2$ Cl_3)

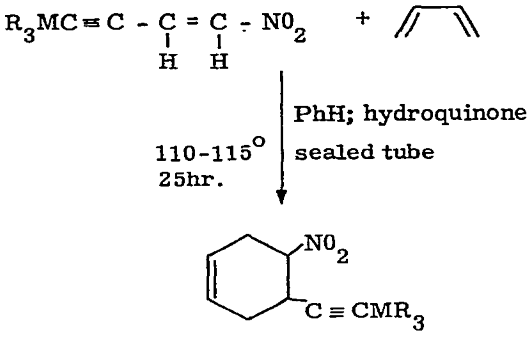
The proportion of terminal attack of methylallene increases in the following order: $Et_2ClGeH < EtCl_2GeH < Cl_3GeH$.

Seyferth and White studied the Diels-Alder reactions of α-pyrone with some Group IV metal substituted acetylenes (129):



(R = R^1 = Me_3Si; R = R^1 = Me_3Ge; R = Me_3Si, R^1 = Me_2HSi, R = Me_3Si, R^1 = Me_3Sn; R = Me_3Si, R^1 = Me_3Ge; R = R^1 = Me_2HSi)
and observed that all except when R = R^1 = Me_3Si and R = Me_3Si, R^1= Me_2HSi gave the expected 1,2-disubstituted benzene product. The two exceptional ones also yielded benzene products containing substantial amounts of the 1,3-disubstituted benzenes, as well as minor amounts of the 1,4-isomers. The formation of these isomers has been shown to result from acid-catalyzed rearrangements of the initially formed 1,2-disubstituted products. The acidic impurities arose from the bromobenzene solvent used. The fact that no rearrangement took place with the other acetylenes is due to the scavenging of acidic impurities which might cause isomerization by the starting acetylene and the benzene product via metal-carbon bond cleavage processes.

The reactions of silicon and germanium containing 1,3-enynic hydrocarbons with a variety of reagents e.g. dienes (130), organocalcium compounds (131) and organosulfenyl halides (132) have been reported. Various reactions are summerized in Chart 16.



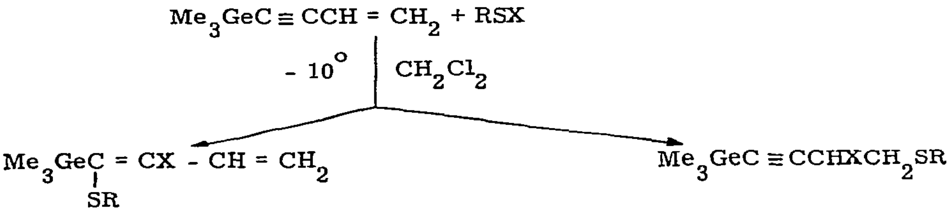
$$R_3MC\equiv C-\underset{H}{\underset{|}{C}}=\underset{H}{\underset{|}{C}}-NO_2 + \text{butadiene} \xrightarrow[110\text{-}115^\circ,\ 25hr.]{PhH;\ hydroquinone,\ sealed\ tube}$$

(60%)

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

$$H_2C=CH-C\equiv C-GeEt_3 + RCaI \xrightarrow{1.\ Et_2O\quad 2.\ H_2O} RCH_2CH=C=CHGeEt_3 \quad + \quad RCH_2CH_2C\equiv CGeEt_3$$

(R = Et, n - Pr, n - Bu; isomer-ratio:- 1 : 1)



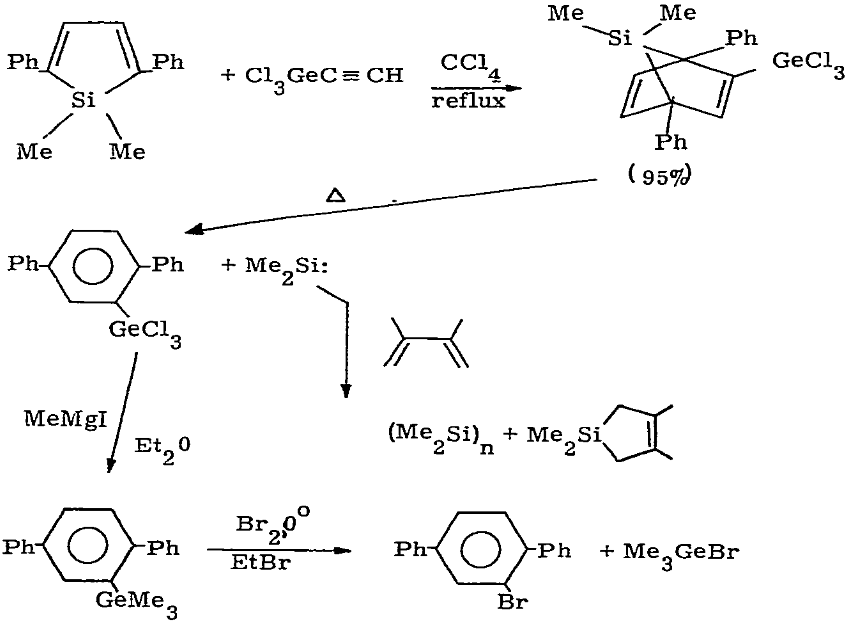
$$Me_3GeC\equiv CCH=CH_2 + RSX \xrightarrow[-10^\circ]{CH_2Cl_2} Me_3Ge\underset{SR}{\underset{|}{C}}=CX-CH=CH_2 \quad + \quad Me_3GeC\equiv CCHXCH_2SR$$

(I) (II)

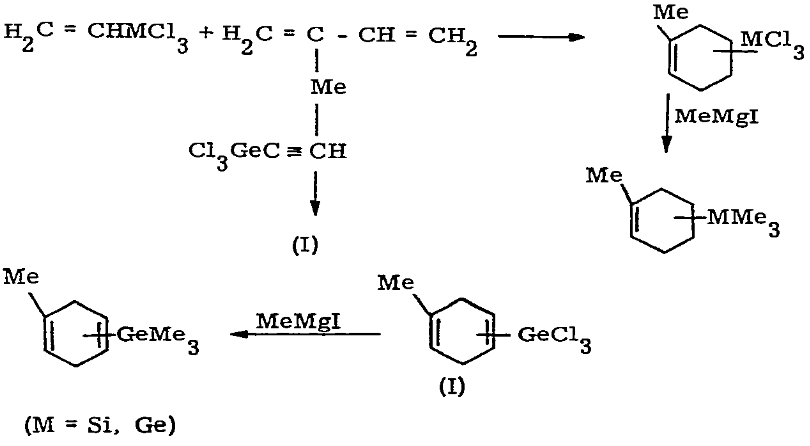
R	X	% yield	
		(I)	(II)
Me	Cl	100	-
Et	Cl	100	-
Me	Br	95	5

Chart 16. Reactions of germanium containing 1,3-enynic hydrocarbons.

Cycloaddition of organometallic dienophiles to 1,1-dimethyl-2,5-diphenylsilacyclopentadiene has been reported to proceed according to the following reaction scheme (133):



Mazerolles et al. synthesized some silicon and germanium containing cyclohexenes and cyclohexadienes via the reaction (134):

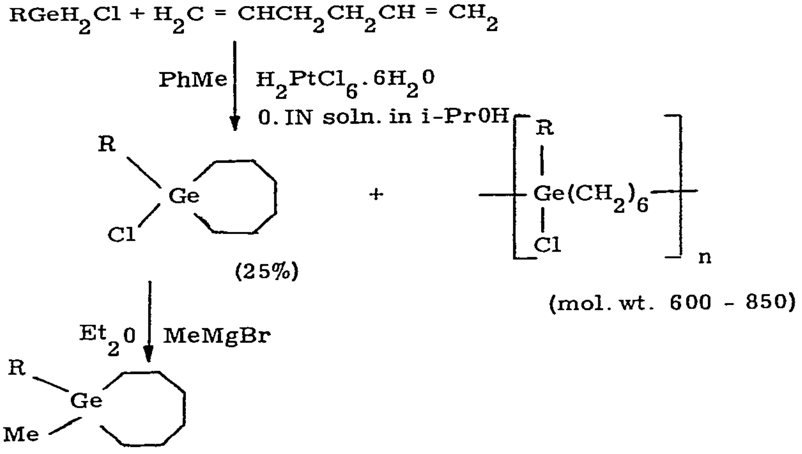


The polymerization of methylvinyloxygermanes, $Me_{4-n}Ge(OCH = CH_2)_n$ (n = 1 - 3) by radical and cationic initiators has been achieved. The radical polymerizations of di- and tri-vinyloxygermanes involved cyclopolymerization with the formation of five- and six-membered rings (135). The preparation of germanium containing copolymers via radical copolymerization of unsaturated germanium containing compounds [e. g. triethyl (methyl) germybutadiene] with vinyl compounds has been patented (136).

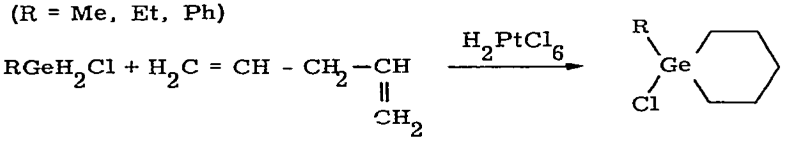
Germacyclanes

An excellent review on the syntheses, reactions and spectroscopy of cyclobutanes containing heterocyclic silicon and germanium (137) has appeared .

Nametkin and coworkers studied the reactions of organohydrohalogermanes with a variety of unsaturated compounds and found these to provide convenient routes to the synthesis of germacyclanes (138, 139):

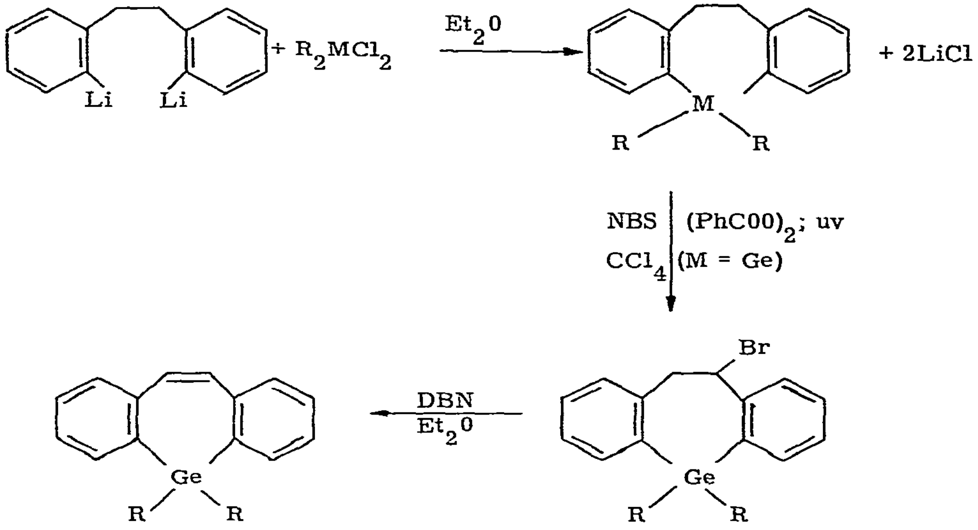


(R = Me, Et, Ph)



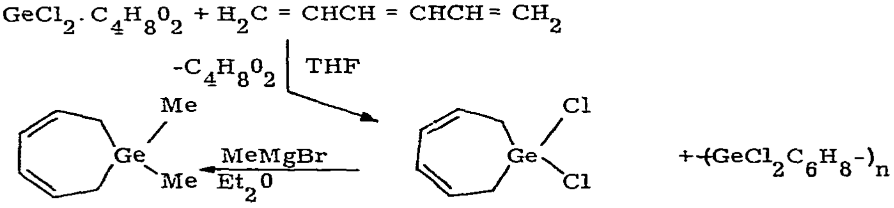
(R = Me, Ph)

The synthesis of 10, 11 - dihydro - 5H - dibenzo[b, f] metallepins has been accomplished by the direct reaction of 2, 2' - dilithiobibenzyl with diorganometal dichlorides (140):



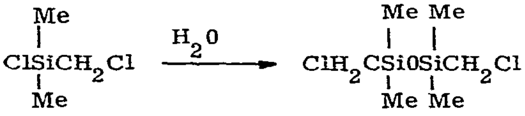
[R = Me, Ph: M = Si, Ge, Sn, Pb; NBS = N-bromosuccinimide; DBN = 1,5-diazabicyclo (4.3.0)non-5ene]

The addition of $GeCl_2$ to dienes (141) and trienes (142) has been used to synthesize germacyclopentenes and germacycloheptadienes:



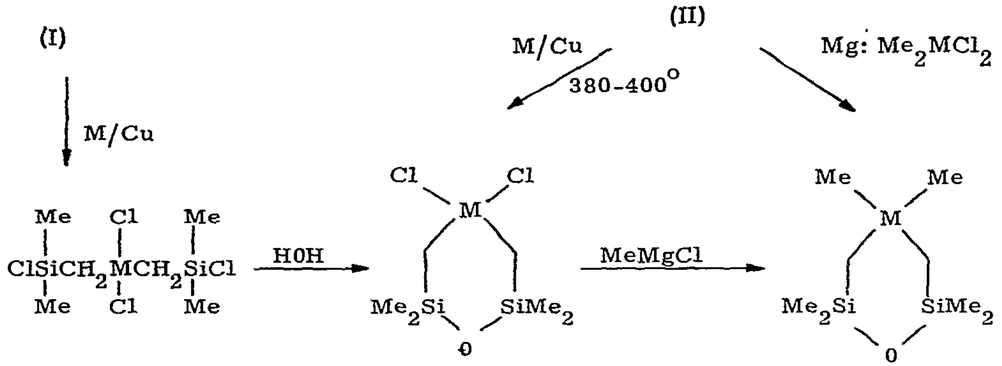
(30-40%)

Mironov et al. reported an excellent method for synthesizing heterocyclic compounds of silicon and germanium via the reaction (143):



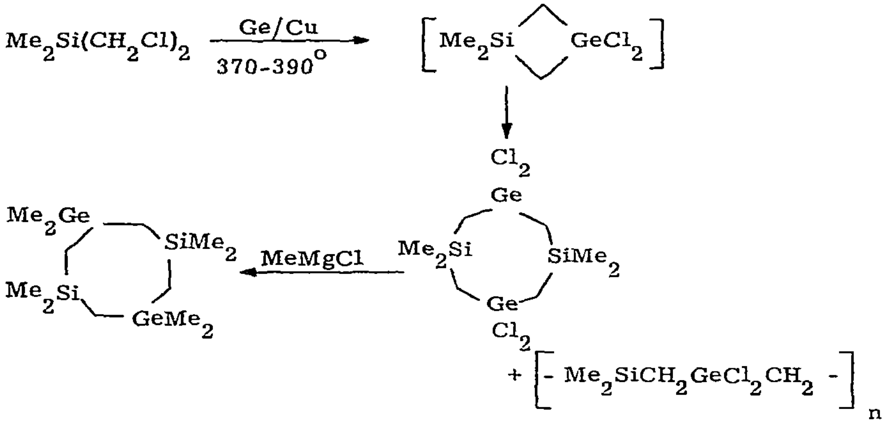
$$\mathrm{Cl\underset{Me}{\overset{Me}{Si}}CH_2Cl} \xrightarrow{H_2O} \mathrm{ClH_2C\underset{Me}{\overset{Me}{Si}}O\underset{Me}{\overset{Me}{Si}}CH_2Cl}$$

(I) (II)

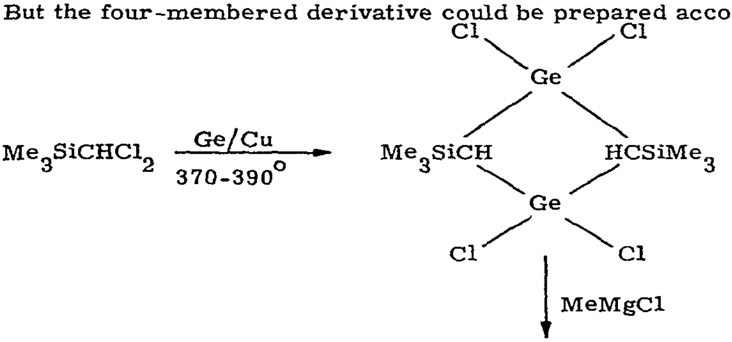


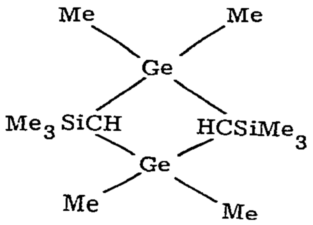
(M = Si, Ge)

An extention of the above method to the attempted preparation of four-membere heterocycle gave only eight-membered heterocycle (144):



But the four-membered derivative could be prepared according to the reaction:





The high stability of the compound may be associated with the steric effect of the trimethylsilyl group.

The preparation and reactions of 1,4-digermacyclohexadienes (145) and 3-germa-bicyclo [3.1.0] hexanes (146) with various substituents at the hetero atom, have been reported. Some of these reactions are given in Chart 17.

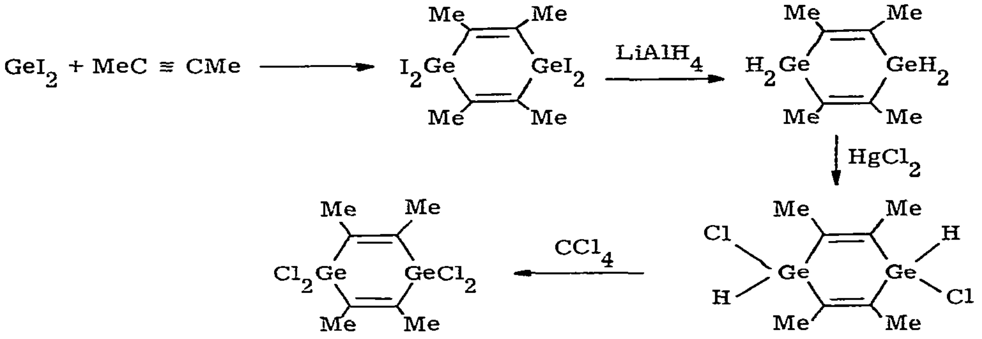


Chart 17. Synthesis of some 1,4-digermacyclohexadienes.

Cohen et al. studied the synthesis and spectroscopic properties of the permethylcyclopolygermanes (147) and observed that the procedure employed for most dependable results involves the rapid addition of dimethyldichlorogerma to a stirred suspension of lithium-dispersion in tetrahydrofuran at room tempera for about four hours. Recrystallization and preparative gas chromatography ga a total yield of 38% which contained the cyclopolygermanes $Me_{10}Ge_5$, $Me_{12}Ge_6$ and $Me_{14}Ge_7$ in a ratio of 1 : 18 : 1.

Carbon - functional germanium compounds

Mazerolles and Cousse investigated some FriedelCraft reactions with germanium containing compounds and observed that the chloro-derivatives of the type $Cl_3Ge(CH_2)_nCl$ react with benzene and toluene according to the scheme (148)

$$\begin{tikzcd}
\mathrm{Cl_3Ge(CH_2)_nCl + PhR} \arrow[rr, "\mathrm{AlCl_3}"] \arrow[d, "\mathrm{AlCl_3}"', "\substack{\mathrm{PhH}\\ (n = 3)}"] \arrow[drr, "\mathrm{AlCl_3};\ (n = 3)", "\mathrm{PhMe}"'] & & \substack{\mathrm{Cl_3Ge(CH_2)_nC_6H_4R}\\ (R = H,\ p - Me;\ n = 0 - 2)} \\
\substack{\mathrm{Cl_3GeCH_2}\underset{\substack{|\\ \mathrm{Me}}}{\mathrm{C}}\mathrm{HPh}\\ + \mathrm{Cl_3Ge(CH_2)_3Ph}} & & \substack{p - \mathrm{Cl_3Ge(CH_2)_3C_6H_4Me}\\ + o - \mathrm{Cl_3Ge(CH_2)_3C_6H_4Me}}
\end{tikzcd}$$

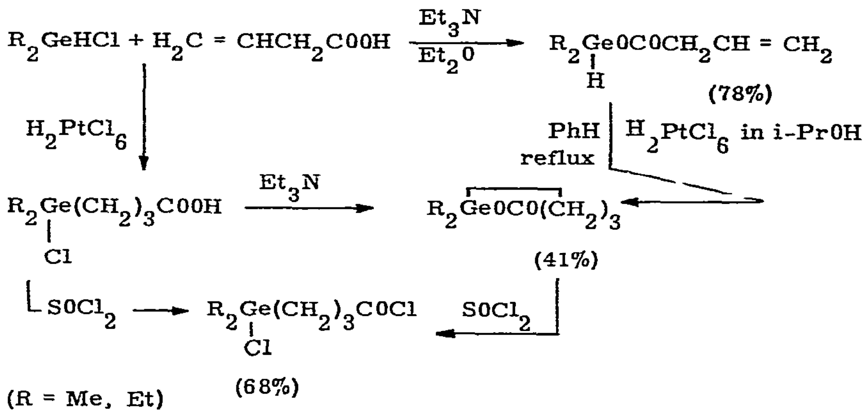
Some trimethylgermyl substituted alcohols (149) and triphenylgermyl substituted esters (150) have been synthesized via the following routes:

$$\begin{tikzcd}
\mathrm{HGeCl_3 + H_2C = CHCH_2Cl} \arrow[r] & \mathrm{Cl(CH_2)_3GeCl_3} \arrow[d, "\mathrm{MeMgCl}"] \\
\mathrm{H0(CH_2)_3GeMe_3} & \mathrm{Cl(CH_2)_3GeMe_3} \arrow[l, "\text{Mg; oxidation}"', "\text{by dry } \mathrm{0_2;H0H}"] \\
\mathrm{Me_3Si0(CH_2)_4Cl + Mg} \arrow[r, "\text{followed by}", "\mathrm{GeCl_4}"'] & \mathrm{Me_3Si0(CH_2)_4GeCl_3} \arrow[dl, "\text{1. MeMgCl}"', "\text{2. Mg; oxidation by dry } \mathrm{0_2;\ H0H}"] \\
\mathrm{H0(CH_2)_4GeMe_3} &
\end{tikzcd}$$

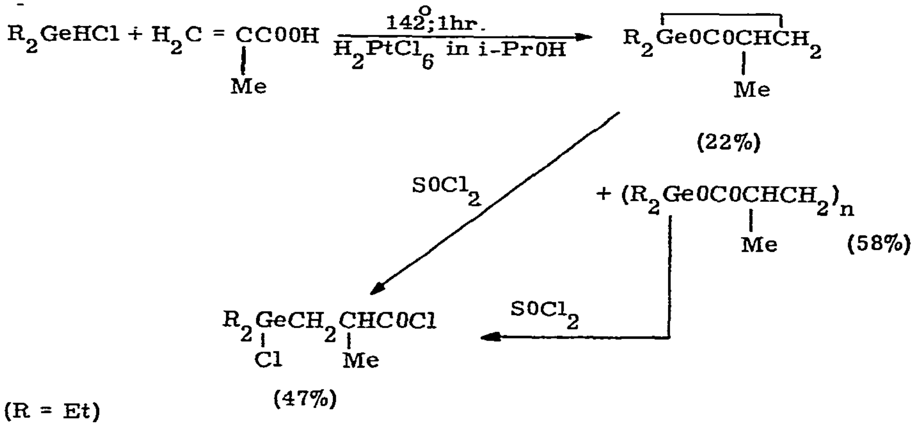
$$\mathrm{Ph_3MX + ZnBrCH_2C00Et} \longrightarrow \underset{(45 - 83\%)}{\mathrm{Ph_3MCH_2C00Et}}$$

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

Germalactones with a -Ge0C0- grouping in the ring could be prepared according to the reactions given below (151):

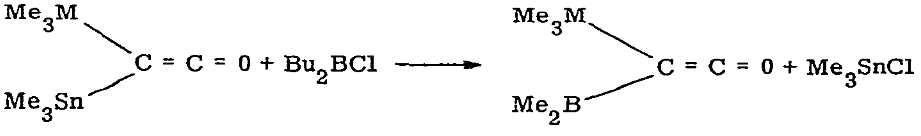


(R = Me, Et)

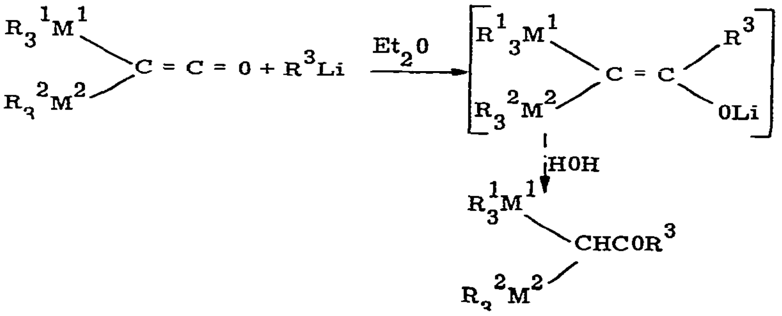


(R = Et)

Ρonomarev and coworkers extended their investigations on the reactions of metalated ketenes (see AS71, p. 156) and reported their reactions with organobor (152) and organolithium (153) derivatives:

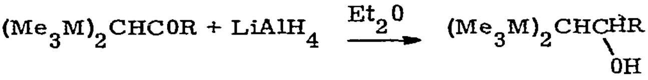


(M = Si, Ge; yield:- 85%)



($M^1 = M^2 = Ge$, $R^1 = R^2 = Me$, Et, Ph, $R^3 = Me$, Bu, Ph; $M^1 = Si$, $M^2 = Ge$, $R^1 = Me$, $R^2 = Me$, Et, $R^3 = Me$)

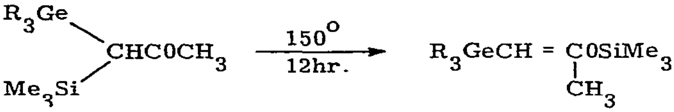
These dimetalated ketones could be reduced to the corresponding alcohols:



$$(Me_3M)_2CHCOR + LiAlH_4 \xrightarrow{Et_2O} (Me_3M)_2CHCH(OH)R$$

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

On heating, these ketones rearrange with the formation of C - germyl - 0 - silyl enols:



$$(R_3Ge)(Me_3Si)CHCOCH_3 \xrightarrow[12hr.]{150^o} R_3GeCH = C(CH_3)OSiMe_3$$

(76%)

(R = Me, Et)

Organometallic enamines have been synthesized according to the reaction (154):

$$MCl_4 + H_2C = C(NMe_2)_2 \longrightarrow Cl_3MCH = C(NMe_2)_2$$

(50%)

(M = Si, Ge, Sn)

Germanium containing polymers

A review on the preparation of Group IV metal (Si, Ge, Sn, Pb) containing polymers by the interfacial technique has appeared (155).

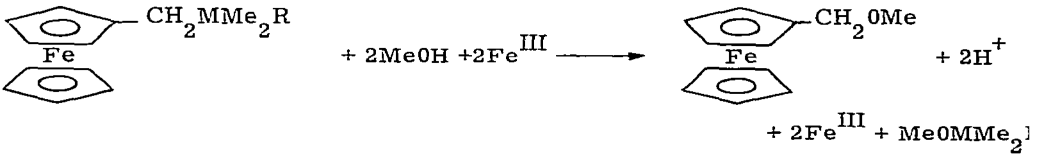
Low molecular weight oligomeric Group IV metal polyesters, $(R_2MOCORCO_2)_n$, have been synthesized by interfacial condensation of Group IV organometallic dihalides with disodium adipate (156, 157). The polymerization rate increases in the order : Si < Ge < Sn as M is varied. Aliphatic - substituted organometallics give higher polymerization rates than aromatic - substituted organometallic compounds (156).

The treatment of poly(acrylamide oxime) with organometallic halides of the type, R_nMCl_{4-n} (R = Pr, Bu, Ph; M = Si, Ge Sn; n = 2, 3), has been shown to give poly (0-acyl amide oximes) containing Group IV metals (158).

Physico - chemical investigations

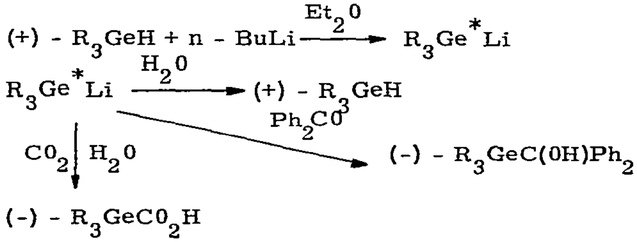
The dipole moments of the allyl derivatives of Group IV elements (C, Si, Ge, Sn) have been calculated and compared to show that as the electronegativity of the element decreases, the inductive effect and dipole moment increase (159).

The rates of cleavage of cinnamyl and benzyl derivatives of silicon, germaniu and tin in strongly basic media indicated that in aqueous and alcoholic dimethyl sulfoxide, the transition states have appreciable carbanionic character especially in the case of the germanium derivatives (160). The metal - carbon bond cleavage of ferrocenylmethyl derivatives of silicon and germanium by methanol in the presence of ferric chloride:

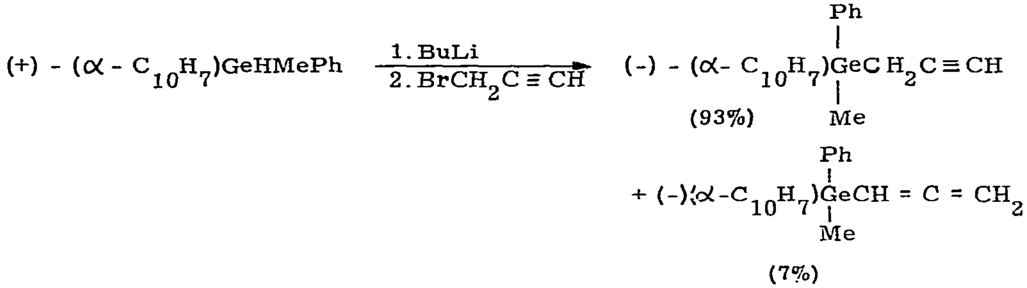


(R = Me, i-Pr; M = Si, Ge)
has been found to be much faster for the germanium analog than for the silicon derivative (161).
Kinetic data for the ozonolysis of derivatives of the type $Et_3M - MEt_3$ (M = Si, Ge, Sn, Pb)(162), oxidation of bis(triethylgermyl)mercury in the presence of tertiary butanol (163), reactions of trityl perchlorate with compounds of the type R_4M(R = Pr, Bu; M = Si, Ge Sn)(164) and the reduction of substituted benzyl chlorides with triethylgermane (165) have been reported.

A number of publications on the reactions of optically active organogermaniu compounds have appeared (166 - 169). Some of these are given in Chart 18.



(R_3 = NpPhEt , Np = 1 $-C_{10}H_7$)



$$(+)\text{-}(\alpha\text{-}C_{10}H_7)GeHMePh \xrightarrow[2.\ BrCH_2C\equiv CH]{1.\ BuLi} (-)\text{-}(\alpha\text{-}C_{10}H_7)\overset{Ph}{\underset{Me}{Ge}}CH_2C\equiv CH \ (93\%) + (-)\text{-}(\alpha\text{-}C_{10}H_7)\overset{Ph}{\underset{Me}{Ge}}CH=C=CH_2 \ (7\%)$$

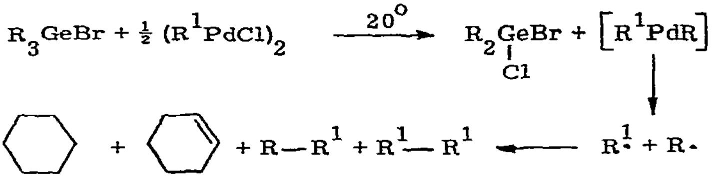
Chart 18. Some reactions of optically active organogermanium compounds.

A study of the photochemistry of a variety of acylmetalloids of the type R_3MCOR^1 (M = Si, Ge) indicated two distinct photochemical pathways : (i) photoisomerization to an oxacarbene ($R_3MO\ddot{C}R^1$), (ii) cleavage of the metalloid-acyl bond (170). The vacuum-ultraviolet photolysis of GeH_4 (171) and the ultraviolet photolysis of H_3GeBr(172) gave free radical species of the type H_3Ge, H_2Ge and H_2GeBr, HGeBr respectively. Structural and bonding properties of these species have been discussed.

The barriers to internal rotation in the molecules of the type $MeMCl_3$ (M = C, Si, Ge, Sn) (173) and the trend in inversion barrier magnitudes within a series of arsines bearing alkyl, silyl, germyl and stannyl groups attached to arsenic (174) have been reported. The heat capacity, the heat of fusion, the temperature of fusion and the calorimetric heat of vaporization have been determined experimentally for tetramethylgermane (175). Agreement between the calculated and experimentally determined entropies requires that the potential barrier to rotation of the methyl groups be 750 $\pm$ 90 cal/mol. This value is surprisingly low considering the trends of the potential barriers in other methyl compounds of the Group IV elements.

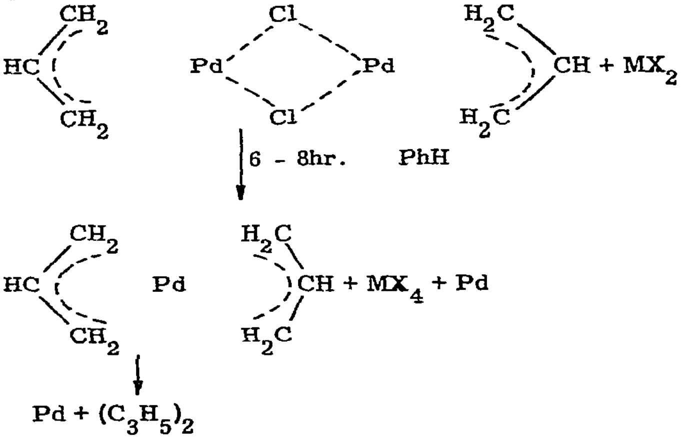
The average energies of dissociation of the metal-nitrogen bond for the compounds of the type Et_3MNEt_2(M = Si, Ge, Sn)(176) and of the oxygen-oxygen bond in organometallic peroxides of the type $R_3MOOCMe_3$ (R = Me, Et; M = Si, Ge, Sn)(177) have been reported. Other topics dealing with the thermochemistry of organogermanium derivatives include: thermal decomposition of germane (178 179); calculation of the heat and entropy of vaporization for dialkyldichlorogermanes and trialkylchlorogermanes(180);the enthalpies of combustion of compounds of the type$(R_3Ge)_2Hg$(R=Et; i-Pr) (181) and heats of hydrolysis and bond energies for compounds of the type Me_3GeX (X = Cl, Br, OEt, SBu, NMe_2)(182).

Domrachev and coworkers reported that although tetraalkyl or tetraaryl derivatives of germanium did not react with bis(allylpalladium chloride)(183) in contrast to the tin and lead derivatives, tricyclohexylgermanium bromide did react as follows (184):



$(R = C_6H_{11}; R^1 = C_3H_5)$

The presence of diallyl and allylcyclohexane is associated with the recombination of the radicals, while the presence of cyclohexene and cyclohexane is associated with the disproportionation of the cyclohexyl radicals. Analogous reaction with germanium dihalides has also been reported (185):



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

Jones et al. studied the ground state properties of Group IV substituted anilines and observed a stabilization of the highest filled molecular orbital for p-trimethylsilyl, and p-trimethylgermyl - N, N - dimethylaniline relative to p-tertiary butyl compound (186). The relative stabilities of the cation radicals of several Group IV substituted anilines have been found to be in the order: p-tertiary butyl -> m-trimethylsilyl->p-trimethylsilyl -> p-trimethylgermyl ->> N, N- dimethylaniline (187).

Some results in the studies of the thermal stability of 0- and C- isomeric elemento-organic derivatives of keto-enol systems, the conditions of the re-arrangement of C-isomers to 0-derivatives and vice versa, as well as effects of migrating group nature or environment on the sense of rearrangement and the electronic effects of substituent connected to the central atom of the keto-enol triads have been reported in two excellent articles (188, 189).

The isomers resulting from hydrogen migration in various silyl- and germyl-cyclopentadienes have been isolated by a Diels-Alder reaction with ethynyltrichlorogermane. The ratio of the isomeric adducts formed is determined both by the heteroatom of the diene and by the alkyl or halogen substituent bonded to the hetero atom (190).

Chvalovský and Včelák studied the directing effects of substituted germyl groups and determined the relative rates of the iron and iodine catalyzed bromination of compounds of the type $PhMe_{3-n}GeCl_n$ ($n = 0 - 3$). The germyl groups were mainly o- and p- directing (191).

The results of pK_a measurements on 4-substituted pyridine N-oxides show that organosilicon and organogermanium substituents are responsible for a decreased basicity relative to the tertiary butyl derivative and the unsubstituted compound (192). The large increase in the rate of protodemetalation reactions of R_3MPh when M is varied from carbon to lead has been attributed to $\sigma - \pi$ conjugation (193, 194).

A general method, based on the principle of the additivity of the properties of chemical bonds, has been proposed for the calculation of the physico-chemical properties of compounds containing Gr. IV elements. The validity of the method has been illustrated by calculating the magnetic susceptibilities of a number of organic compounds of the above elements using the equation obtained. The agreement between the calculated and experimental magnetic susceptibilities has been shown to be satisfactory (195).

Some other studies include: low temperature polarization of C, Si, Ge and

B alkoxides (196); solubilities and medium effects of Ph_4M (M = C, Si, Ge) in acetonitrile, methanol and some ethanol-water solvents (197); intramolecular coordination in organic derivatives of the elements (198); kinetics, mechanism and stereochemistry of nucleophilic substitution at Si, Ge and Sn (199); calculation of average molecular polarizability for alkylgermanes (200); polarographic behaviour of ethyltrichlorogermane (201); reactivity of organic derivatives of elements with halogenomethanes (202); conformational equilibria of Group IV organometallic compounds (203); atomic polarization of C, Si and Ge alkoxides (204); mean amplitudes of vibration for $H_3GeC \equiv CH$ (205); calculation of the solubility of germanium in gaseous mixture of Ge - Cl - H (206) and acid catalyzed isomerization of 1,2-bis(trimethylsilyl) benzene and related compounds (207).

Spectral studies

A number of general articles on the spectroscopy of organometallic compound (including those of germanium) have appeared (208 - 214).

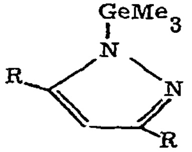
IR and Raman studies

Vyazankin and coworkers reviewed the results of certain spectroscopic (IR and N studies on $d_\pi - p_\pi$ interaction in organic compounds of Group IV elements (215). The authors also used infrared spectroscopy to study the basicity of the derivativ of the type $(Et_3M)_2X$ (M = Si, Ge; X = O, S, Se, Te) and observed the basicity to increase with M in the order: Si < Ge < Sn (216). Infrared spectroscopy has also been used to study the basicities (217) and the effects of $d_\pi - p_\pi$ and σ, π conjugation(218) in alkenyl derivatives of silicon and germanium. A study of the basicity of oxygen atoms in the series of alkoxygermanes employing infrared spectroscopy indicated that germanium forms weaker $d_\pi - p_\pi$ bonds with oxygen than does silicon (219). The relative basicity of (dimethylamino) chlorogermane $(Me_2N)_{4-n}GeCl_n$ (n = 1-3), as determined by infrared spectroscopy has been sho to decrease with increasing number of chlorine atoms in the molecule (220).

The presence of rotational isomerism around the Fe - Ge bond in derivatives of the type : π- $C_5H_5(CO)_2FeGeCl_2R$ (R = Me Et, n-Pr i - Pr) and π- C_5H_5 — $(CO)_2FeGeX_2Me$ (X = Cl, Br, I) has been demonstrated by infrared spectroscopy The enthalpy differences of the rotational isomers were calculated and the less polar trans - isomer was shown to be more stable (221). Durig and Turner recorded the infrared and Raman data for p-chlorophenylgermane and p-fluorophenylgermane (222). The vapour phase spectra indicated the germyl group to be freely rotating for these molecules. The vibrational spectra of compounds of the type $(PhCH_2)_4M$(M = Ge, Sn) have been discussed in view of the occurrence of rotational isomers and interactions between the benzyl group and the rest of the molecule (223). More specific studies include the following compounds : MX_4(M = Ge, Sn; X = Cl, Br)(224); Me_3GeF (225); $MeGeH_2X$ (X = F, Cl, Br, I)(226); GeH_4(227); $Br_3GeGeBr_3$(15); $Me_2MB_{10}H_{12}$(M = Ge, Sn)(60); μ- $MR_3C_2B_4H_7$(R = H, Me; M = Si, Ge)(59); $Ph_3MMn(C0)_4L$ and $Ph_3MMn(C0)_3L_2$ (M = Si, Ge, Sn; L = PPh_3; L_2 = dipy., diphos) (66); $H_3GeMn(C0)_5$(68); $C_5H_5M(C0)_nGeX_3$(M = Fe, n = 2; M = Ni, n = 1; X = Cl, Br, I) (70); $[\pi\text{-}C_5H_5Fe(C0)_2]_2GeI_2$(72); $(H_3Ge)_2Fe(C0)_4$(73); π - $C_5H_5(C0)_2FeGe(0Me)_3$ (74); $H_3GeCo(C0)_4$(76); $Me_2Ge(N_2RR^1R^2)_2$ (R groups = H, Me, $SiMe_3$; $GeMe_3$) (80); $Me_2NN(R)C(Y)YMMe_3$(R = H, Me; M = Si, Ge; Y = 0, S) (81); Me_2Ge — $(N0_3)_2$ (228); N - phenyl and N - cyclohexyl organogermazanes (229); germanium containing phenols (90); germanium arsines (100); $(RS)_4M$ (R = Me, Et, Pr; M = C, Si, Ge, Sn)(230); n - $BuSeMR_3$ (R = Me, Et, n - Bu, Ph; M = Si, Ge, Sn) (116); $(Me-C\equiv C)_4M$(M = Si, Ge, Pb) (231); HGe $(C\equiv CH)_3$ (232); compounds containing heterocyclic germanium (93, 140, 142, 143); permethylcyclopolygermanes (147); 1- germalactones (151); metalated ketenes (153); Et_3MCH_2C00Me (M = Si, Ge, Sn)(233) and germanium and tin carbonyls (234).

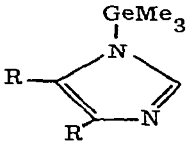
NMR studies

On the basis of PMR data (studied at various temperatures), a metallotropic rearrangement has been shown to occur in metal cyclopentadienyls: $Me_3MC_5H_5$ (M = Si, Ge) (235, 236); $(Me_3M)_2C_5H_4$ (M = Si, Ge, Sn) (237, 238) and $H_3GeC_5H_4Me$ (239). Cotton and Ciappenelli used PMR spectroscopy to establish a fast intramolecular metallotropic rearrangement of the Me_3Ge group from N to N in compounds (I) and (II) but not in (III) and (IV) (240).



(I) R = H

(II) R = Me



(III) R = H

(IV) R = Me

The high resolution NMR spectra of certain Group IV allyl compounds, $R_3M(CH_2)_nCH = CH_2R^1$(R = Me, Et, Ph; R^1 = H, Ph; M = Si, Ge, Sn; n = 1 or 2) have been studied in an attempt to detect manifestations of ground state $p_\pi - d_\pi$ overlap. The conclusions reached do not support the existence of such an overlap (241). On the basis of ^{31}P - NMR chemical shifts of $(R_3M)_nPX_{3-n}$ (R = H, Me, Bu, Ph; X = H, Me, Ph; M = Si, Ge, Sn) it has been shown that in both the Ge - P and the Sn - P bond $\left[P(3p) \longrightarrow M\ (nd)\right]\pi$ - interactions play an important role, which is not found for the Si - P bond (242). Chipperfield et al. interpreted the PMR spectra of p-substituted phenoxysilanes and phenoxygermanes to show that in these compounds the Si - 0 bond has more $p_\pi - d_\pi$ character than the Ge - 0 bond, but that $p_\pi - d_\pi$ bonding is not negligible in phenoxygermanes (243). The ^{19}F - NMR spectra for substituted α- and β-fluoronaphthalenes with metallo substituents of the type MR_3 (M = Group IV metalloid; R = Me) in the 4, 6 and 7 positions have been recorded. The ^{19}F substituent chemical shift data provide evidence for $d_\pi - p_\pi$ conjugative electron withdrawal in the ground state by the metalloidal substituents (244). The acidities of some aryl-substituted germanes in liquid ammonia (245) and redistribution equilibria of the substitutents Cl, Br and I and Cl, Br, I and 0Ph between the methylsilicon and methylgermanium moities (246) have been studied by PMR spectroscopy. It has been shown that the internal chemical shift of the ethyl protons for derivatives of the type Et_4M(M = Si, Ge, Sn) increases in the transition from inert to solvating solvents (247).

The liquid phase hydrogenation of cyclopentadienyltriethylgermane (248), the addition reactions of heptamethylsilagermazane with isocyanates or isothiocyanates (85) and the addition - elimination reactions of heptamethyldigermazane or hexamethyldigermoxane with phenyl isothiocyanate (86) have been studied using NMR spectroscopy. Satgé and coworkers studied the addition of germylphosphines to several ethylenic compounds using NMR spectroscopy (92, 95). Other studies and articles include : ^{73}Ge spectra of R_4Ge (R = Me, Et, Pr, Bu)(249); NMR spectra of the lithium salts of the triphenyl substituted Group IV metal anions (250); exchange reations of bromodifluorophosphine with silyl and germyl derivatives of Group VI elements (251); ^{19}F - NMR spectra of some metallomethyl substituted fluoroaromatic compounds (252) and NMR spectroscopy of organometallic allyl derivatives (253).

More specific studies include the following compounds: $X_3MC_6H_4F$ (M = Si, Ge; X = F, Cl, Br) (254); *organosilyl- and organogermyl-substituted ferrocenes* (52, 53); $Me_3GeC_2Me_2B_4H_5$ (58); μ - $MR_3C_2B_4H_7$ (R = H, Me; M = Si, Ge)(59); $Me_2MB_{10}H_{12}$ (M = Ge, Sn)(60); $(C_5H_5)_2M(Cl)M^1Ph_3$ (M = Zr, Hf; M^1 = Si, Ge) (65); $H_3GeMn(C0)_5$(68); $C_5H_5M(C0)_nGeX_3$ (M = Fe, n = 2; M = Ni, n = 1; X = Cl Br, I)(70); $X_3MMn(C0)_4$(X_3M = Ph_3Ge, Ph_3Sn, Ph_3Pb, Cl_3Sn)(255); $[\pi - C_5H_5Fe(C0)_2]_2GeI_2$(72); $(H_3Ge)_2Fe(C0)_4$(73); π -$C_5H_5(C0)_2FeGe(0Me)_3$(74); $H_3GeCo(C0)_4$(76); $Me_2NN(R)C(Y)YMMe_3$(R = H, Me, $SiMe_3$; M = Si, Ge; Y = 0, S) (81); $Me_2Ge(N_2RR^1R^2)_2$(*R groups = H, Me, SiMe$_3$, GeMe$_3$*)(80); $Me_3M\underset{\underset{H}{|}}{P}Ph$ (M = C, Si, Ge Sn)(256); germanium arsines (100); $Me_2\underset{\underset{X}{|}}{Ge}CH = CH_2$(X = Br, I)(18); Ph_3MX (M = Group IV element; X = phenyl, vinyl or azido group)(257); germanium heterocyclic compounds (93, 140 ,142 144, 147); 1-germalactones (151); metalated ketenes (153) and $Me_3M(CH_2)_n0H$ (M = C , Si, Ge; n = 1-4)(258).

Miscellaneous

The photoelectron spectra of MF_4 (M = C, Si, Ge) and Me_4M(M = C, Si, Ge, Sn, Pb) have been obtained by using a double - focusing electron spectrometer (259, 260). Stabilization of certain molecular orbitals in both series of compounds has been shown to be in accord with the presence of back bonding into 'd' orbitals and its increasing importance with the increasing atomic number of the central atom. Evans and coworkers reported the helium -(I) photoelectron spectra of the species Me_4M(M = C, Si, Ge, Sn, Pb). The spectra of Si, Ge and Sn compounds are very similar, although strikingly different from the spectrum of neopentane (261). Other publications on photoelectron spectroscopy include: compounds of the type: MH_4(M = C, Si, Ge, Sn)(262); RQ (R = H, Me, H_3Si, H_3Ge, Me_3Si; Q = NC0, NCS, N_3)(263); $(H_3M)_2Y$ and H_3MSH(M = C, Si, Ge; Y = 0, S, Se, Te) (264); $(H_3Ge)_3X$(X = N, P) and H_3MPH_2(M = C, Si, Ge)(265) and

(266).

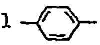
Microwave spectroscopic measurements have been made on halogermanes (267, 268) and vinylgermane (269). The results have been used to calculate various structural parameters. Normal coordinate analysis has been carried out for $Cl_3MCo(C0)_4$ (M = Si ,Ge, Sn)(270) and Ge_2H_6(271). Murdoch et al.

used the sector-microphotometer method of electron diffraction to determine the gas phase structures of digermyl selenide (272) and germyl pseudohalides (273).

A computer program has been designed to calculate theoretical values for the relative intensities of the mass spectrum peaks for compounds containing any number of and any combination of the elements, C, H, 0, N, S, Si and Ge (274). Nametkin and coworkers studied the mass spectra of a number of sila- and germa-cyclanes (275) and observed that the spectra of the germanium compounds with respect to the silicon compounds are enriched by light fragment ions and exhibit lower intensities of odd-electron ions . Mass spectroscopic data have been reported for following compounds: M_2R_6(R = Ph; M = C, Si, Ge, Sn, Pb)(276); $Me_3GeC_2Me_2B_4H_5$(58); μ-$MR_3C_2B_4H_7$(R = H, Me; M = Si, Ge) (59); $Me_2MB_{10}H_{12}$(M = Ge, Sn)(60); $(C_5H_5)_2M(Cl)M^1Ph_3$(M = Zr, Hf; M^1 = Si, Ge, Sn) (65); $H_3GeMn(C0)_5$(68); $(H_3Ge)_2Fe(C0)_4$(73); $H_3GeCo(C0)_4$(76); $Me_2Ge(N_2RR^1R^2)_2$ (R groups = H, Me, $SiMe_3$, $GeMe_3$)(80); germanium heterocyclic compounds (140, 147, 277, 278) and organochlorogermanes (279).

The charge-transfer interactions between NbF_5, MoF_6 and WF_6 and the Group IV compounds R_4M(M = Si, Ge, Sn; R = alkyl) have been studied using UV spectroscopy (280). The UV spectral data have been reported for a number of germacyclanes (142, 147).

Electron paramagnetic resonance spectroscopy has been used to measure the bimolecular rate constants for the self-reactions of methyl radicals and of radicals with the structures $Me_3\dot{M}$, $Me_3M\dot{C}H_2$, $Me_3M\dot{M}Me_2$ and Me MMMe - $\dot{C}H_2$ (M = C, Si, Ge, Sn) in ditertiary butyl peroxide as solvent (281). The electronic effects of β- Si, Ge and Sn substituents on alkyl radicals (282) and evidence against $d(\pi) - p(\pi)$ bonding in radicals of the type $R_2\dot{C}XR_3$(283) (X = Group IV or group V element) have been presented on the basis of ESR data. Electron spin resonance spectra are reported for a number of organosilyl- and organogermyl-substituted benzenes and alkyl-benzenes. The ESR spectra of organometal-substituted alkyl-benzenes indicate that organometal substituents exert greater influence on the electronic distribution in the molecule than do the alkyl substituents (284).

The ^{35}Cl - NQR data for compounds of the type: Cl  MMe_3(M = C, Si, Ge, Sn) (285) and R_3MCH_2Cl(R = H, alkyl, alkoxy, CH_2Cl, Cl; M = C, Si, Ge, Sn) (286) have been reported.

The reports regarding structural data for various organogermanium compounds include: X-ray diffraction study of π-(C_4H_6) π-$C_5H_5FeGe(Me)Cl_2$ (287); crystal structure of $\{\pi\text{-}C_5H_5Co(CO)\}_2(GeCl_2)_2Fe(CO)_4$(288); (Fig. 3); crystal and molecular structure of $Ru(CO)_4(GeCl_3)_2$ (289); crystal chemistry of tetraphenyl derivatives of Group IV elements (290, 291); crystal data for compounds of the type: $Me_2M(CN)_2$ (M = Si, Ge, Sn, Pb)(292) and lattice parameters and space groups of the acetates of Group IV elements (293).

Analysis and applications

A number of methods for the determination of germanium in organogermanium compounds have been reported (294-296).

Various claims regarding applications of organogermanium compounds include: germane oligomer $(GeH_2)_x$ or $(GeH)_x$ in textile and fibre technology (297); $(Me_2CHCH_2CH_2)_4Ge$ in depositing a coating of germanium (298); possible application of the crystals of Ph_4M(M = Si, Ge, Sn, Pb) in quantum electronic devices (299) and carboxyethyl germanium sesquioxide in promoting the growth of rice (300).

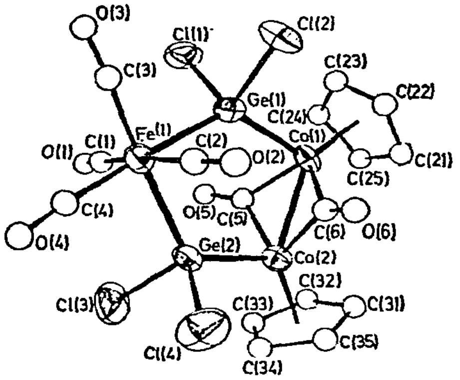


Fig. 3. The molecular structure of $\{\pi\text{-}C_5H_5Co(CO)\}_2(GeCl_2)_2Fe(CO)_4$

[from M. Elder and W.L. Hutcheon; J.Chem.Soc., Dalton Trans.(1972)175]

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