GERMANIUM

ANNUAL SURVEY COVERING THE YEAR 1971

Bhuvan C. Pant

Department of Chemistry, The University of Aston in Birmingham,
Gosta Green, Birmingham B47ET, (England)

CONTENTS

Books and reviews

A monograph entitled 'The Organic Compounds of Germanium' has appeared (1). The authors have described from a critical point of view the chemistry of organogermanium derivatives and have included complete literature references through 1968 and many references from 1969. In a book series 'Organometallic Reactions', organogermanium compounds have been included (2).

Lesbre has reviewed some aspects of germanium chemistry with particular emphasis on the variable polarity of the germanium atom in its organometallic compounds (3). In a review article Neumann discussed the recent developments in the field of organic derivatives of Group IVB elements including those of germanium (4). Few other review articles (5 - 8) which cover broad aspects of organogermanium chemistry have appeared.

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

Direct syntheses and germanium-halogen compounds

The direct synthesis of alkyltrihalogermanes has been achieved by the reaction between germanium powder and higher alkyl halides in an evacuated ampule (9):

$$RBr + Ge \xrightarrow[13\ hrs.]{220 - 240^{o}} RGeBr_3$$

$(R{=}C_4H_9,\ C_6H_{13},\ C_8H_{17})$

Zueva et al. continued their investigations on the direct synthesis of lower trialkylhalogermanes and patented (10) the method involving the reaction between elemental germanium and an appropriate alkyl halide at high temperature in the presence of copper and a mixture of trivalent metal, such as gallium and aluminium.

A number of organoiodogermanes have been prepared in considerably higher yields by passing gaseous hydrogen iodide through organochlorogermanes (11):

$$R_nGeCl_{4-n} + (4-n)HI \longrightarrow R_nGeI_{4-n} + (4-n)HCl$$

$$[R_nGeI_{4-n} = Me_3GeI\ (83^{o}/o),\ EtGeI_3(98^{o}/o)$$
$$PhGeI_3\ (75^{o}/o),\ Me_2Ge(I)CH_2I\ (75^{o}/o)]$$

Another route involves boiling germanium tetraiodide with alkyl iodides in the presence of stoichiometric amount of copper powder:

$$GeI_4 + RI \xrightarrow[PhMe,\,8hr.]{Cu} RGeI_3$$

$$[R = Me(50^{\circ}/o),\ Pr(16^{\circ}/o),\ CH_2I(20^{\circ}/o)]$$

The authors also found that the direct synthesis of organoiodogermanes, usually conducted in the gas phase, may in some cases be carried out in liquid phase e.g.

$$Ge + C_8H_{17}I \xrightarrow{boiled} C_8H_{17}GeI_3\ (25^{\circ}/o)$$

The insertion of germylenes of the type $GeCl_2$: on the tetrahalogenated compounds of Group IVB elements has been reported to proceed via an intermediate polyhalogenated derivative with a germanium-metal bond followed by an exchange reaction to the dihalides (12):

$$GeCl_2{:} + MX_4 \longrightarrow Cl_2Ge(X)MX_3 \longrightarrow Cl_2GeX_2 + MX_2$$

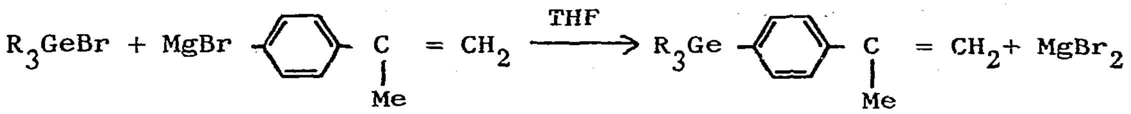
$$(X = Cl\ ;\ M = C,\ Ge,\ Sn)$$

The formation of polyhalogenated products has been proved by treating the product with a Grignard reagent:

$$Cl_2Ge{:} + GeCl_4 \rightleftharpoons [Cl_3Ge - GeCl_3] \xrightarrow{-20^{\circ};\ EtMgBr} Et_3GeGeEt_3 + Et_4Ge + Et_3GeH + (Et_2Ge)_n.$$

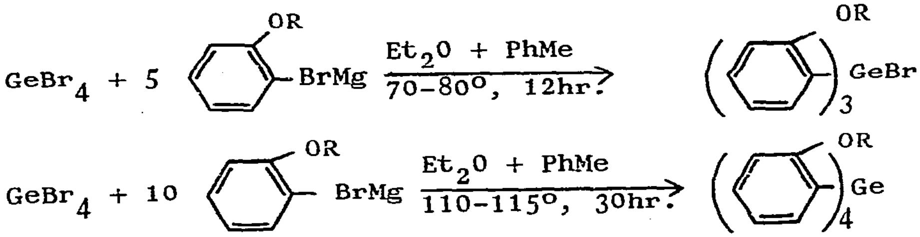
Alkylation and arylation

Some germyl-substituted benzenes have been synthesized by the conventional Grignard procedure (13):

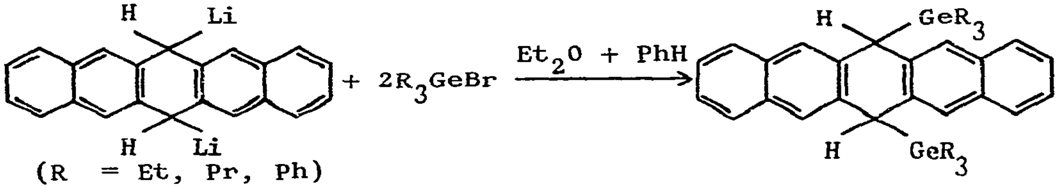


(R = Pr, i-Pr, n-Bu and i-Bu)

The conditions have been studied for the reactions of germanium tetrabromide with bromo (O-alkoxyphenyl) magnesium, which lead to the tetrakis - and bromotris - derivatives of germanium (14):



Organogermanium derivatives of pentacene could be synthesized according to the reaction (15):



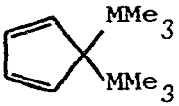
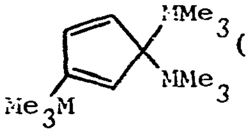
Zueva et al. reported the methylation of dimethyldicloro-germane with alkyl halides in the presence of a mixture of aluminum and copper to be a simple and efficient method for preparing trimethylchlorogermane (16):

$$Me_2GeCl_2 + RCl \xrightarrow[390 - 400^{\circ}]{Al + Cu} Me_3GeCl$$

(R = Me, Et, Pr)

Thus ethyl chloride and propyl chloride must undergo thermal decomposition under the reaction conditions.

A number of polymetallated cyclopentadienes of the type:

 or  (M and M^1 = Si, Ge, Sn, same or different)

have been synthesized (17):

$$C_5H_5MMe_3 + BuLi + Me_3M^1Cl \longrightarrow Me_3MC_5H_4M^1Me_3 + LiCl$$

(M = Si, Ge and M^1 = Si, Ge, Sn)

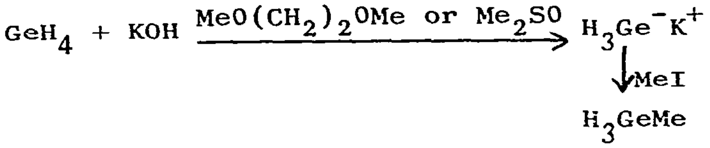
$$C_{11}H_{22}SiGe + (CH_3)_3SnN(C_2H_5)_2 \longrightarrow C_{14}H_{30}SiGeSn + (C_2H_5)_2NH$$

NMR and mass spectra verified the structure of the compounds.

Germanium-hydrogen compounds

The recent investigations into the syntheses and chemical properties of the ions BH_3CN^-, $H_3GeBH_3^-$ etc. have been covered in a brief review (18). Van Dyke reviewed the procedures used in the preparation of inorganic derivatives of GeH_4 and Ge_2H_6 (19). Syntheses and properties of some organogermanium hydrides have been the subject of two Ph.D. theses (20, 21).

Jolly et al. reported that germane in contact with solid potassium hydroxide gave the deprotonated anion intermediate (22):



$$\begin{array}{l} GeH_4 + KOH \xrightarrow{MeO(CH_2)_2OMe \text{ or } Me_2SO} H_3Ge^-K^+ \\ \qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad \downarrow MeI \\ \qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad H_3GeMe \end{array}$$

Stannic chloride has been found to be an excellent reagent for the chlorination of silanes and germanes (23):

$$GeH_4 + SnCl_4 \xrightarrow{\text{room temp}} H_3Ge\,Cl + SnCl_2 + HCl$$

$$Ge_2H_6 + SnCl_4 \xrightarrow[\text{10min.}]{\text{room temp}} Ge_2H_5Cl + Ge_2H_4Cl_2 + HCl$$

Further investigation by Mironov et al. indicated that the reaction of organogermanium hydrides with stannic chloride proceeds over a broad range of temperatures (even at -70^{o}) yielding organochlorogermanes (24):

$$R_nGeH_{4-n} + SnCl_4 \xrightarrow{ROR} R_nGeH_{3-n}Cl + nR_2O \cdot HSnCl_3$$

(R=alkyl, aryl, alkenyl etc; n=0, 1 or 2)

Mironov et al. extended their studies on the reactions of trihalogermanes and observed that primary alkyl iodides condense with these and their ether complexes to give alkyltrihalogermanes (25, 26):

$$HGeX_3 + RI \xrightarrow[-HI]{R^1{}_2O} RGeX_3 + RGeX_nI_{3-n}$$

(R = Me, Et, Pr, Bu etc; R^1 = Me, Et, Bu; X = Cl, Br)

Partial exchange of halogens between $HGeX_3$ and the liberated acid has been reported and the effect of various organic groups on the yields discussed.

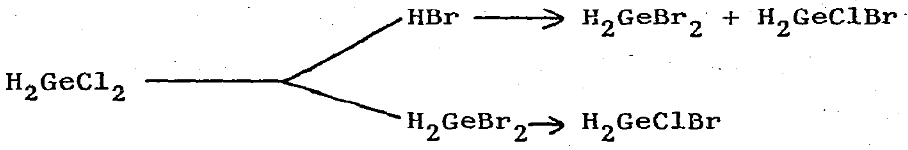
The reaction of trihalogermanes with ammonia and amines has been shown to give complexes of the type $R_nNH_{4-n}GeX_3$ ($n = 0 - 4$; X = F, Cl, Br) with a salt like structure. These undergo reactions of the type (27):

$$Et_3NHGeCl_3 + RI \longrightarrow Et_3NHI + RGeCl_3$$

(R = Me, Pr etc.)

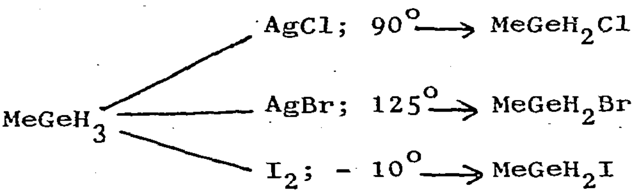
$$Et_3NHGeBr_3 + CH_2 = CHCH_2Br \longrightarrow CH_2 = CHCH_2GeBr_3 + Et_3NHBr$$

Barker and Drake studied various exchange reactions of dihalogenogermanes using ^1H - NMR technique (28):



$$H_3GeCl + BBr_3 \longrightarrow H_3GeBr + H_2GeBr_2 + H_2GeClBr$$

Some monohalo derivatives of methyl germane have been synthesized (29):



Organofluorogermanes, on the other hand could be synthesized by the reaction (30):

$$2RR^1GeHBr + PbF_2 \longrightarrow 2RR^1GeHF + PbBr_2$$

$(R = Me;\ R^1 = Me \text{ or } H)$

Fehér and Plichta reported the synthesis of some organodigermanium hydrides (31). The reactions are compiled in Chart 1.

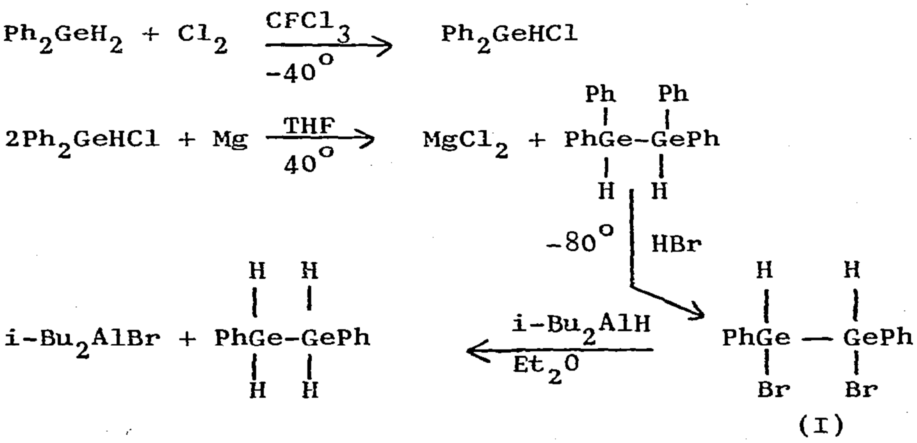
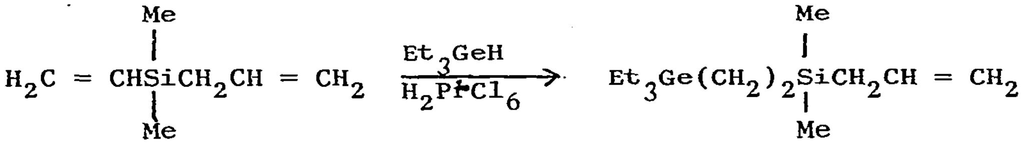


Chart 1. Synthesis of some organodigermanium hydrides.

The compound (I) has been claimed by the authors to be the first digermanium hydride existing in dl and meso forms due to asymmetric germanium atoms.

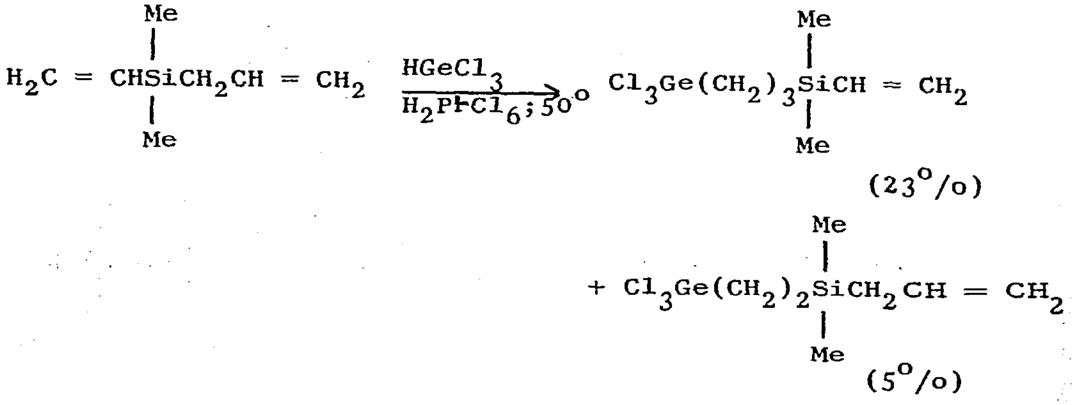
The gas-phase reaction of dimethyldihydrogermane with 2,3 - $C_2B_4H_8$[2,3 - dicarbahexaborane (8)] gave a number of volatile methyl carboranes as well as a dark reddish-brown polymeric solid whose composition corresponds to $(GeMe)_n$(32). The investigation indicated the pronounced tendency of dimethyldihydrogermane to lose methyl groups. Nametkin and coworkers reported the formation of oligomers and six-membered cyclogermanium products in the reaction of $RGeH_2Cl$ (R = Me or Ph) with 1, 4-pentadiene (33).

The selective addition of triethylgermane to the vinyl group of allylvinylsilanes:



$$H_2C = CH\underset{Me}{\overset{Me}{Si}}CH_2CH = CH_2 \xrightarrow[H_2PtCl_6]{Et_3GeH} Et_3Ge(CH_2)_2\underset{Me}{\overset{Me}{Si}}CH_2CH = CH_2$$

has been proposed to have a radical character (34). The preferential addition of trichlorogermane proceeds as:

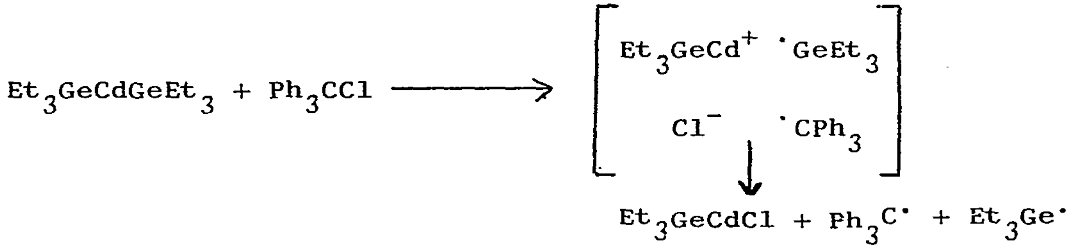


$$H_2C = CH\underset{Me}{\overset{Me}{Si}}CH_2CH = CH_2 \xrightarrow[H_2PtCl_6;\,50^o]{HGeCl_3} Cl_3Ge(CH_2)_3\underset{Me}{\overset{Me}{Si}}CH = CH_2 \quad (23^o/o)$$

$$+\ Cl_3Ge(CH_2)_2\underset{Me}{\overset{Me}{Si}}CH_2CH = CH_2 \quad (5^o/o)$$

Germanium-metal compounds

A review article on dimetallic compounds e.g. organic Ge-Cd, Ge-Hg, Ge-Zn, Si-Hg etc. derivatives has appeared (35). The reactions of bis(triethylgermyl) cadmium with trityl chloride, benzyl bromide, and allyl iodide in 1:1 molar ratio in aprotic solvents have been found to proceed through the selective cleavage of the Ge-Cd-Ge linkage (36,37). The proposed reaction scheme is compiled in Chart 2.



$$Et_3GeCdGeEt_3 + Ph_3CCl \longrightarrow \left[\begin{array}{cc} Et_3GeCd^+ & {}^{\cdot}GeEt_3 \\ Cl^- & {}^{\cdot}CPh_3 \end{array}\right] \downarrow Et_3GeCdCl + Ph_3C^{\cdot} + Et_3Ge^{\cdot}$$

$$Et_3Ge^{\cdot} + R \longrightarrow Et_3GeR (R = Et_3Ge \text{ or } Ph_3C)$$

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

$$Et_3GeCdCl \longrightarrow Cd + Et_3GeCl$$

The overall reaction could be written as:

$$(Et_3Ge)_2Cd + Ph_3CCl \xrightarrow{PhMe} \underset{(100^{o}/o)}{Cd} + \underset{(43^{o}/o)}{Et_3GeCl} + \underset{(48^{o}/o)}{Et_6Ge_2} + \underset{(28^{o}/o)}{Et_3GeCPh_3}$$

+ trityl radicals (detected by esr)

Chart 2. Reaction of bis(triethylgermyl) cadmium.

The synthesis of a new germyl-mercury compound has been accomplished via the reaction (38):

$$[(Me_3Si)_2N]_2Hg + (Et_3Ge)_2Hg \xrightarrow[100^{o};\,6hr.]{THF} Et_3GeHgN(SiMe_3)_2$$

Vyazankin et al. reported the syntheses and reactions of chalcogen-containing silyl - and germyl-mercury compounds (39,40):

$$(R_3M)_2Hg + {}^1/_8\ X_8 \xrightarrow[\text{hexane}]{\text{pentane or}} R_3M - X - Hg - MR_3$$

$(R = Et \text{ or } i\text{-}Pr;\quad M = Si,\ Ge;\quad X = S,\ Se)$

$$R_3M - X - Hg - MR_3 \xrightarrow[\text{pentane}]{h\nu} R_3MXMR_3 + Hg$$

$$i\text{-}Pr_3GeSHgGePr_3\text{-}i \xrightarrow[40^{o}]{\text{Li; THF}} i\text{-}Pr_3GeLi + i\text{-}Pr_3GeSLi + Hg$$

Under similar conditions tellurium reacted as:

$$(Et_3Ge)_2Hg + Te \xrightarrow{\text{pentane}} Hg + HgTe + (Et_3Ge)_2Te + Et_6Ge_2$$

$$(88^{o}/o)(15^{o}/o)(58^{o}/o) \qquad (39^{o}/o)$$

The photolytic decomposition of $(Me_3M)_2Hg(M = Si,Ge)$ in benzene and toluene indicated less aromatic substitution in the case of the germanium than the silicon radicals. The results being consistent with the lower strength of the germanium-carbon than of the silicon-carbon bond (41). Various products are listed in Table 1.

The reaction between organic dibromo compounds and bis(trimethylgermyl) mercury has been studied (42):

$$(Me_3Ge)_2Hg + Br(CH_2)_2Br \xrightarrow{-20^{o}} Hg + 2Me_3GeBr + H_2C = CH_2$$

Glushakova and Aleksandrov extended their investigations on the oxidation of germyl-mercury compounds and reported the rapid oxidation of bis(triphenylgermyl) mercury to proceed via the scheme (43):

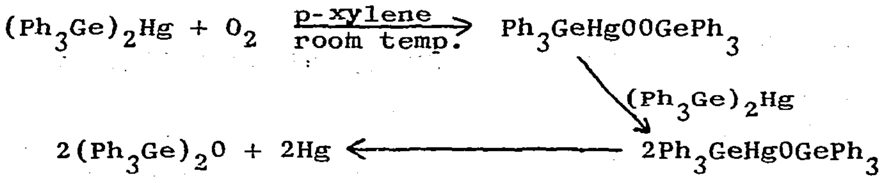


Table 1. Photolytic decomposition of bis(trimethylgermyl) mercury.

In benzene		In toluene	
At 40°	At 180°	At 40°	At 180°
Hg(100°/o) Me_6Ge_2(98°/o) Me_3GePh(1°/o) 2,5-cyclohexadienyltrimethylgermane (trace) Me_3GeH(trace) High boiling products (ca. 1°/o)	Hg(100°/o) Me_6Ge_2(99°/o)	Hg(100°/o) Me_6Ge_2(96°/o) $MeC_6H_4GeMe_3$ (1°/o) $PhCH_2GeMe_3$ (1°/o) High boiling products(ca. (1°/o)	Hg(100°/o) Me_6Ge_2(98°/o) $PhCH_2GeMe_3$ (0.5°/o) Dibenzyl(trace) High boiling products (ca.1°/o)

Some exchange reactions of bis(triethylgermyl) mercury with organostannanes (44) and with organomercury compounds (45) have been reported:

$$(Et_3Ge)_2Hg + Et_3SnX \xrightarrow[100^{o};\,10-14hr.]{THF\ or\ PhMe} Hg + Et_3GeX + Et_3GeSnEt_3$$

$$(X = MeO,\ EtO,\ Et_2N)$$

$$(Et_3Ge)_2Hg + R_2Hg \xrightarrow{THF} [2Et_3GeHgR] \longrightarrow 2Hg + 2Et_3GeR$$

$$(R = CH_2COOMe,\ CH_2COEt,\ C_6F_5\ ,CN)$$

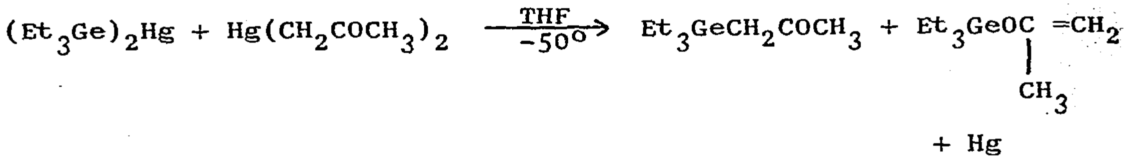
The results obtained (46, 47) in the study of the reactions of bis(triethylgermyl) mercury with organomercury compounds are compiled in Chart 3.

$$(Et_3Ge)_2Hg + ClHgR \longrightarrow Et_3GeHgCl + Et_3GeHgR$$

$$Et_3GeHgCl \longrightarrow Et_3GeCl + Hg$$

$$Et_3GeHgR \longrightarrow Et_3GeR + Hg$$

$(R = CHFCOOEt,\ CF_2COOEt,\ CFClCOOEt)$



$$(Et_3Ge)_2Hg + Hg(CH_2COCH_3)_2 \xrightarrow[-50^o]{THF} Et_3GeCH_2COCH_3 + Et_3GeOC(CH_3){=}CH_2 + Hg$$

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

The most satisfactory method for the preparation of trialkylgermyl alkali metal compounds (in quantitative yields) has been reported to be the one involving the reaction (48):

$$R_3GeGeR_3 + 2M \xrightarrow[\text{room temp.}]{HMPT} 2R_3GeM$$

$(R = Me,\ Et,\ Pr,\ Bu;\quad M = Li,\ Na,\ K)$

Conductivity measurments indicated triethylgermylpotassium (at least in HMPT) to behave as a strong electrolyte. According to the authors when considering the physical and chemical properties of trialkylgermyl alkali metal compounds in HMPT, account must be taken of their virtually ionic structure . The reactions of triethylgermylpotassium with a variety of organic and inorganic reagents have been reported (49):

$$2Et_3GeK + O_2 \longrightarrow 2Et_3GeOK \xrightarrow[HOH]{NH_4Cl} (Et_3Ge)_2O + H_2O$$

$$Et_3GeK + CO_2 \xrightarrow[\text{acidification}]{\text{followed by careful}} Et_3GeCOOH$$

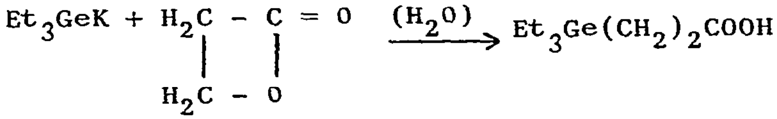
$$\downarrow 100^{o}$$

$$(Et_3Ge)_2O + H_2O + 2CO$$

$$2Et_3GeK + CH_2Cl_2 \longrightarrow (Et_3Ge)_2CH_2 + 2KCl$$

$$Et_3GeK + GeI_2 \xrightarrow[\text{by MeI}]{\text{followd}} (Et_3Ge)_3GeMe$$

$$Et_3GeK + H_2C = 0 \xrightarrow{(H_2O)} Et_3GeCH_2OH$$



$$Et_3GeK + \begin{array}{l} H_2C - C = 0 \\ \;|\qquad\;\; | \\ H_2C - 0 \end{array} \xrightarrow{(H_2O)} Et_3Ge(CH_2)_2COOH$$

West and Sandman observed an unexpected reaction between triphenylgermane and dimsyl-sodium or - potassium (50):

$$\underset{}{Ph_3GeH} + \underset{(I)}{MeSOCH_2^{-}Na^{+}} \longrightarrow Ph_3GeNa$$

$$Ph_3GeNa + MeSOCH_2^{-}\ Na^{+} \xrightarrow[85-90^{o};\ 4hr.]{DMSO} \underset{(II)}{Ph_3GeMe} + \underset{(III)}{Ph_3GeSMe}$$

$$+ \underset{\text{(small amounts)}}{(Ph_3Ge)_2O}$$

The relative amounts of (II) and (III) have been shown to depend on the concentration of (I).

Some reactions of the metal - metal bonded compounds of Group IVB elements have been studied (51, 52):

$$Me_3GeGeMe_3 \xrightarrow{ICl} Me_3GeI + Me_3GeCl + I_2$$

$$Me_3GeGeMe_3 \xrightarrow{Br_2} 2Me_3GeBr$$

$$Me_3GeGeMe_3 \xrightarrow{I_2} 2Me_3GeI$$

$$Me_3GeSnMe_3 \xrightarrow{ICl} Me_3GeCl + Me_3SnI$$

$$Me_3GeSnMe_3 \xrightarrow{HCl} Me_3GeCl + Me_3SnCl + CH_4 + H_2 + Me_3GeSn(Me_2)Cl$$

$$Me_3GeSnMe_3 \xrightarrow{CF_3I} Me_3GeI + Me_3SnF + Me_4Sn + CH_4 + Sn + \text{fluorocarbons}$$

The order of reactivity towards HCl and ICl has been shown to be: Sn-Ge > Sn-Si >> Ge-Si > Ge-Ge > Si-Si.

Wallbridge and Savory synthesized a new class of small nido-carborane compounds containing a stable B - MMe_3 - B (M = Si, Ge) three-center bond via the reaction (53):

$$Me_3MCl + Na^+C_2Me_2B_4H_5 \xrightarrow[25^o]{Et_2O} Me_3MC_2Me_2B_4H_5 + NaCl \quad .$$

No isomerization (at 25°) to the termal isomers has been observed.

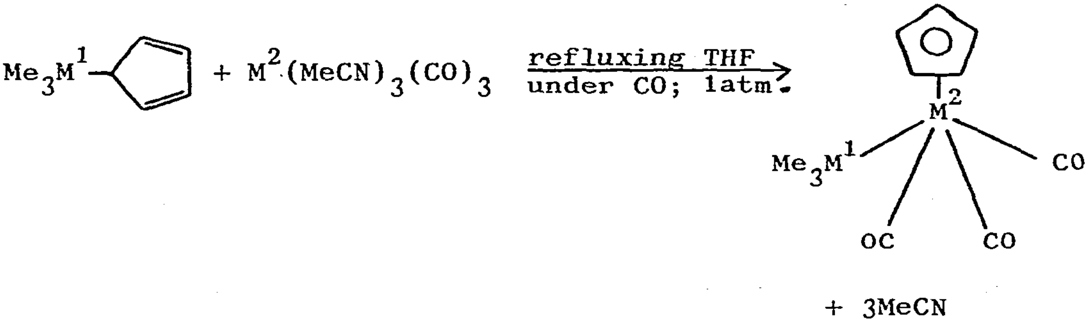
Various preparative routes for the transition metal-Group IVB compounds have been reviewed (54). Organogermyltitanium dialkylamides have been synthesized and characterized by using various spectral data (55):

$$Ph_3GeH + BuLi \xrightarrow{Et_2O} Ph_3GeLi + BuH$$

$$Ph_3GeLi + BrTi(NR_2)_3 \longrightarrow Ph_3GeTi(NR_2)_3 + LiBr$$

$$2Ph_3GeLi + Br_2Ti(NR_2)_2 \longrightarrow (Ph_3Ge)_2Ti(NR)_2 + 2LiBr$$

Lappert and Keppie extended their studies on the oxidative addition of cyclopentadienyl (trimethyl) metallanes of the group IVB elements to coordinately unsaturated transition metal substrates. Most of the reactions studied could be represented as (56):



(M^1 = Ge, Sn; M^2 = Cr, Mo, W)

The authors found the reactivity to decrease for a given M^1 in the sequence $Cr > Mo \approx W$ and $Sn > Ge >> Si$ (unreactive) for a given M^2. A number of synthetic routes have been reported for the preparation of Ge-Cr, Ge-Mo and Ge-W complexes (57-59). Some of these are compiled in Chart 4.

$$(Et_3Ge)_2Hg + [C_5H_5Cr(CO)_3]_2Hg \xrightarrow{20^o} Hg + Et_3GeCr(CO)_3C_5H_5$$

(80°/o) (40°/o)

$$C_5H_5Mo(CO)_3GeCl_3 + 3AgBF_4 \xrightarrow[15\ min.]{Me_2CO} 3AgCl + 3BF_3 + C_5H_5Mo(CO)_3GeF_3$$

(80°/o)

Chart 4. Synthesis of some germanium-transition metal complexes.

Marks accomplished the synthesis of extremely air-sensitive, tetrahydrofuran adduct of dimethylgermylene - pentacarbonylchromium complex via the reaction (60):

$$Me_2GeCl_2 + Na_2Cr_2(CO)_{10} \xrightarrow[-78^o]{THF} Me_2GeCr(CO)_5 + NaCl + NaCr(CO)_5Cl$$

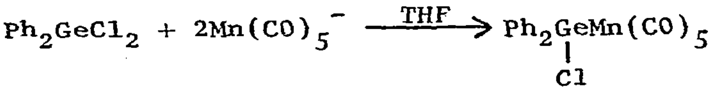
The synthesis of germanium-manganese complexes could be achieved by the photochemical reaction of MCl_3^- (M = Ge,Sn) anion with cyclopentadienylmanganese derivatives (61):

$$C_5H_5Mn(CO)_3 + THF \xrightarrow{hv} C_5H_5Mn(CO)_2 \cdot THF$$

$$C_5H_5Mn(CO)_2 \cdot THF + MCl_3^- \longrightarrow C_5H_5Mn(CO)_2MCl_3^- + THF$$

$$Mn_2(CO)_{10} + MCl_3^- \xrightarrow[CH_2Cl_2]{hv} Mn_2(CO)_9MCl_3^- + CO$$

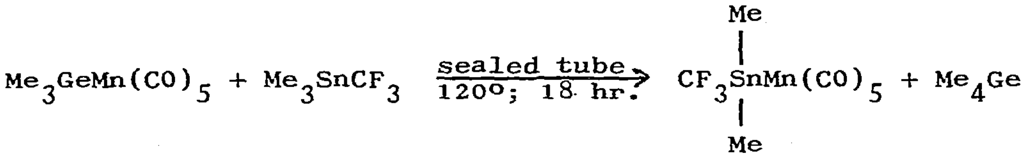
The final product of the reaction between diphenyldihalogermane and $Mn(CO)_5^-$ has been found to depend upon the halogen (62):



$$Ph_2GeCl_2 + 2Mn(CO)_5^- \xrightarrow{THF} Ph_2\underset{\substack{| \\ Cl}}{Ge}Mn(CO)_5$$

$$Ph_2GeBr_2 + 2Mn(CO)_5^- \xrightarrow{THF} Ph_2Ge[Mn(CO)_5]_2$$

Clark and Hunter observed a new type of exchange reaction involving metal-metal bond cleavage(63):



$$Me_3GeMn(CO)_5 + Me_3SnCF_3 \xrightarrow[120^o;\ 18\ hr.]{sealed\ tube} CF_3\overset{\substack{Me \\ |}}{\underset{\substack{| \\ Me}}{Sn}}Mn(CO)_5 + Me_4Ge$$

The preparation and properties of a number of Group IVB metal-tricarbonylnitrosyliron derivatives have been described (64,65):

$$Ph_3GeBr + Na[Fe(CO)_2(NO)\{P(OPh_3)\}]$$

$$\downarrow Et_2O$$

$$Ph_3Ge[Fe(CO)_2(NO)\{P(OPh_3)\}] + NaBr$$

$$R_3GeX + Na[Fe(CO)_3NO] \xrightarrow{Et_2O} R_3Ge[Fe(CO)_3NO] + NaX$$

$(R = Ph, Cl; X = Cl, Br)$

Stone and Knox synthesized a number of Ge-Ru and Ge-Os complexes and studied their reactions (66, 67). Some of their results are compiled in Chart 5.

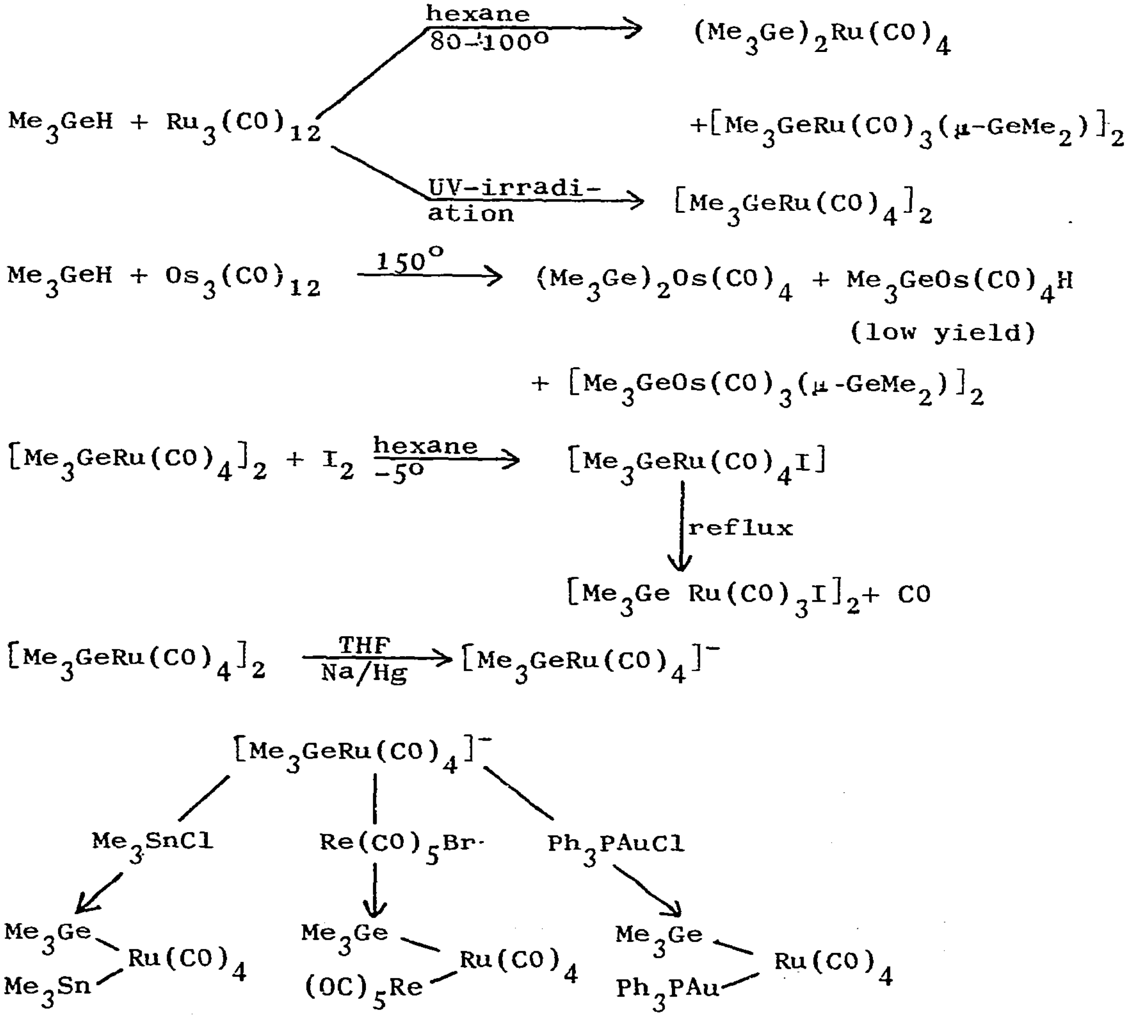


Chart 5. Synthesis and reactions of Ge-Ru compounds.

Various derivatives of transition metal carbonyl compounds have been shown to react with bis(triphenylgermyl) mercury thus providing convenient route to germanium-transition metal compounds (68):

$$\begin{array}{l}(Ph_3Ge)_2Hg + [M(CO)_n(C_5H_5-\pi)_m]_2 \\ \qquad\qquad 60\text{-}100^{\circ}\Big\downarrow MePh \\ Hg + 2Ph_3GeM(CO)_n(C_5H_5-\pi)_m\end{array}$$

$$\left[\begin{array}{l}M = Fe,\ n = 2,\ m = 1 \\ M = Co,\ n = 4,\ m = 0 \\ M = Ni,\ n = m = 1\end{array}\right]$$

$$(Ph_3Ge)_2Hg + ClFe(CO)_2(C_5H_5) \xrightarrow{100^{\circ}} Ph_3GeFe(CO)_2C_5H_5 + Ph_3GeCl$$

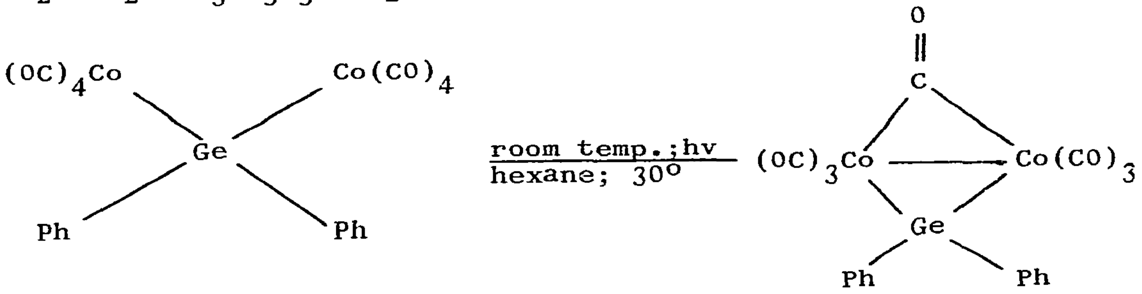
Ogino and Brown observed the reactions of $Cl_3MCo(CO)_4$ (M = Ge,Sn) systems with some nucleophiles to result in displacement of CO, in coordination at cobalt or in heterolytic rupture of the M-Co bond to produce ionic species of the type (69):

$$[MCl_3L_n]^+[Co(CO)_4]^- \quad \text{or} \quad MCl_3^-[CoL_n(CO)_{5-n}]^+$$

$$(M = Ge,\ Sn;\ L = Bu_3P,\ Ph_3P)$$

Photochemical reactions of some germanium-transition metal derivatives have been investigated (70):

$$\begin{tikzcd} Ph_2Ge[Fe(CO)_2(C_5H_5\ -\pi)]_2 \arrow[d, "\text{irradiated for 45 min.}", "\text{hexane } 25^{o}"'] \\ Ph_2GeFe_2(CO)_3(C_5H_5\ -\pi)_2 + CO \end{tikzcd}$$

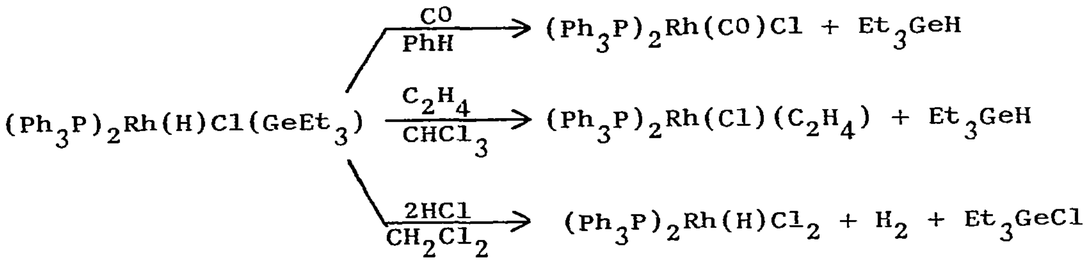


Glockling and Hill extended their studies on the synthesis of germanium-rhodium complexes by oxidative addition reactions in the presence of large excess of organogermane (71):

$$(Ph_3M)_3RhCl + R_3GeH \rightleftharpoons (Ph_3M)_2Rh(H)Cl(GeR_3) + Ph_3M$$

$(M = P,\ As;\ R = Me,\ Et,\ Cl)$

Some reactions of these complexes are compiled in Chart 6.



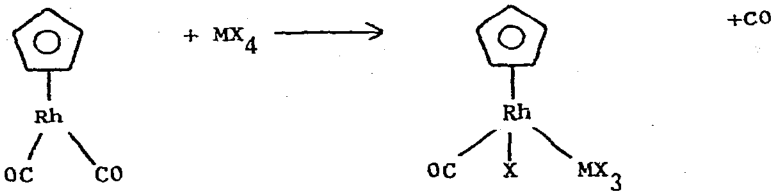
$$(Ph_3P)_2Rh(H)Cl(GeEt_3) \xrightarrow[PhH]{CO} (Ph_3P)_2Rh(CO)Cl + Et_3GeH$$

$$(Ph_3P)_2Rh(H)Cl(GeEt_3) \xrightarrow[CHCl_3]{C_2H_4} (Ph_3P)_2Rh(Cl)(C_2H_4) + Et_3GeH$$

$$(Ph_3P)_2Rh(H)Cl(GeEt_3) \xrightarrow[CH_2Cl_2]{2HCl} (Ph_3P)_2Rh(H)Cl_2 + H_2 + Et_3GeCl$$

Chart 6. Some reactions of Ge-Rh complexes.

The synthesis of germanium-rhodium derivatives has also been accomplished via the reaction (72):



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

Hooton reported the preparation of a germanium-iridium complex according to the reaction (73):

$$\text{trans- Ir(Et}_3\text{P)}_2\text{(CO)Cl} + 2\text{(Me}_3\text{Ge)}_2\text{Hg} \xrightarrow[\text{PhH}]{\text{reflux}} \underset{\text{(I)}}{\text{Ir(HgGeMe}_3\text{)(GeMe}_3\text{)}_2\text{(Et}_3\text{P)}_2\text{(Co)}} + \text{Hg} + \text{Me}_3\text{GeCl}$$

The author observed a ready cleavage of Hg-Ge bond in reactions of the type:

$$\text{(I)} \quad + \text{HCl} \xrightarrow{\text{PhH}} \underset{\text{(II)}}{\text{Ir(HgCl)(GeMe}_3\text{)}_2\text{(Et}_3\text{P)}_2\text{CO}} + \text{H}_2 + \text{Me}_3\text{GeCl}$$

$$\text{(II)} \quad + \text{HCl} \xrightarrow[\text{days}]{\text{several}} \text{Ir(Et}_3\text{P)}_2\text{Cl}_2\text{H(CO)} + \text{H}_2 + \text{Hg} + 2\text{Me}_3\text{Ge}$$

$$\text{(I)} \quad + \text{Br(CH}_2\text{)}_2\text{Br} \xrightarrow[\text{temp.}]{\text{room}} \underset{\text{(III)}}{\text{Ir(HgBr)(GeMe}_3\text{)}_2\text{(Et}_3\text{P)}_2\text{CO}} + \text{C}_2\text{H}_4 + \text{Me}_3\text{GeBr}$$

$$\text{(III)} + \text{Br(CH}_2\text{)}_2\text{Br} \xrightarrow[\text{hrs.}]{\text{several}} \text{Ir(HgBr)Br}_2\text{(Et}_3\text{P)}_2\text{CO} + 2\text{Me}_3\text{GeBr} + 2\text{C}_2\text{H}_4$$

A germanium-nickel complex has been prepared via the reaction (74):

$$(Et_3Ge)_2Hg + \pi\text{-}C_5H_5(PPh_3)NiCl \xrightarrow[\text{PhH}]{20^{\circ};\ 1\ \text{hr.}} Hg + Et_3GeCl + Et_3GeNi(PPh_3)C_5H_5\text{-}\pi$$

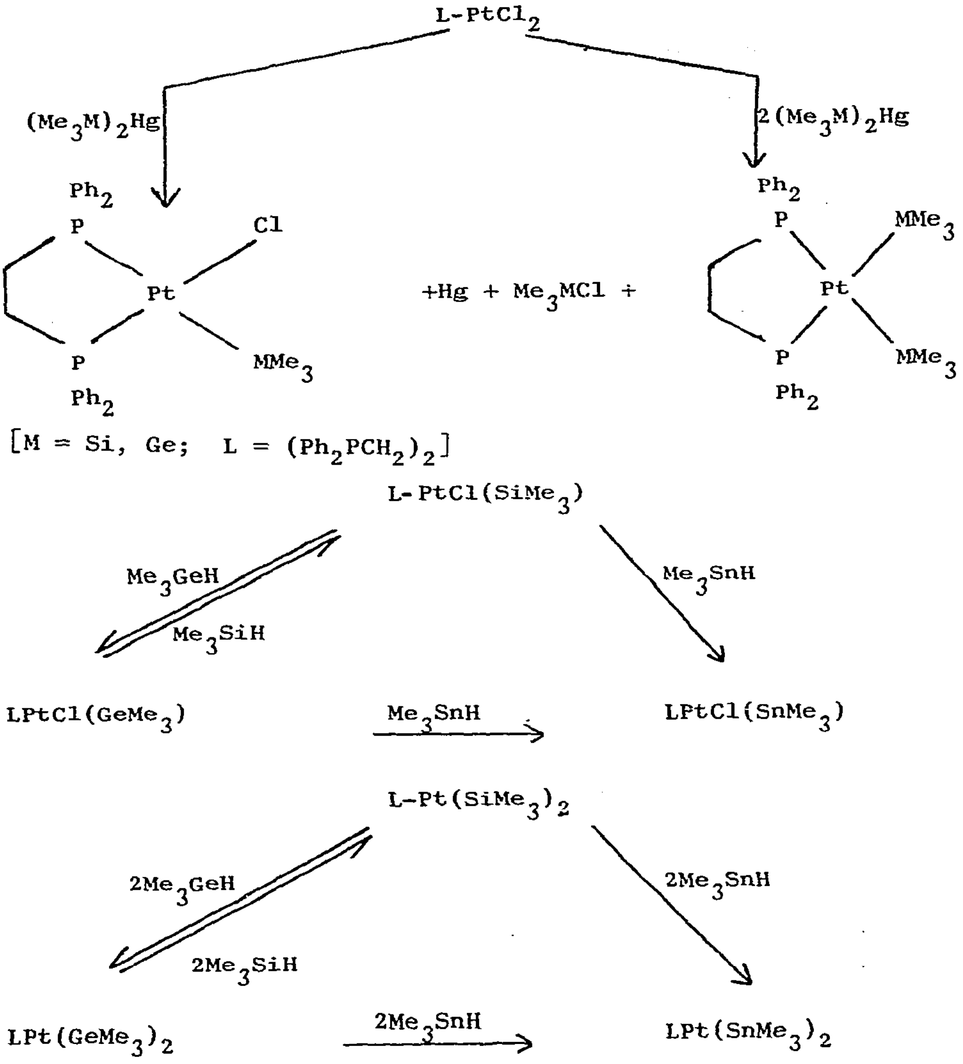


Chart 7. Synthesis and reactions of Ge - Pt complexes.

The preparation, reactivity, chemical bonding and structure of Group IVB metal-platinum bonded complexes have been reviewed (75). On the basis of ^1H-NMR studies four different species of the type $HPt(PEt_3)_2(GeH_2Cl)_n(GeHCl_2)_{3-n}$ (n = 1-3) have been shown to form in the reaction between trans - $ClPt(PEt_3)H$ and H_3GeCl (76,77). Glockling and Clemmit continued their investigations on the synthesis and exchange reactions of silyl - and germyl-platinum complexes (78). Various reactions are listed in Chart 7.

The position of equilibrium favouring R_3M products was found to be in the order Sn >> Ge > Si.

Germanium-nitrogen compounds

The hydrazine derivatives of Group IVB elements have been synthesized (79) according to the reaction scheme given in Chart 8.

$$3Me_3MNMe_2 + N_2H_4 \longrightarrow (Me_3M)_2N - NH(MMe_3) + 3HNMe_2$$

(M = Si, Ge, Sn)

$$\begin{tikzcd}
Me_3MCl + N_2H_4 \arrow[r] & Me_3M \leftarrow N_2H_4Cl \; (M = C, Si, Ge, Sn) \arrow[d, "N_2H_4"] \\
 & (Me_3M)NHNH_2 + N_2H_5Cl
\end{tikzcd}$$

(M = C, Si)

$$\begin{tikzcd}
Me_3CNHNH_2 \arrow[r, "1.BuLi", "2.Me_3MCl"'] & Me_3CNHNHMMe_3 \arrow[d, "\substack{1.BuLi \\ 2.Me_3MCl}"] \\
 & Me_3CNHN(MMe_3)_2
\end{tikzcd}$$

(M = Si, Ge, Sn)

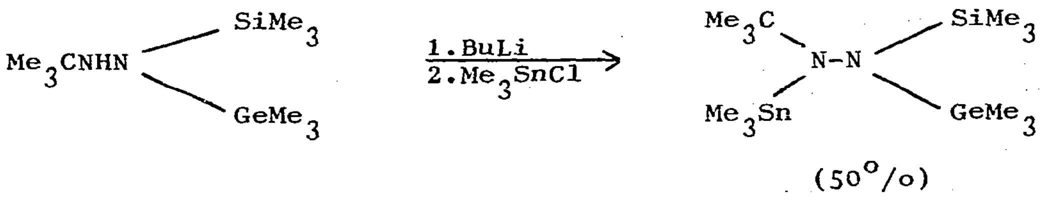
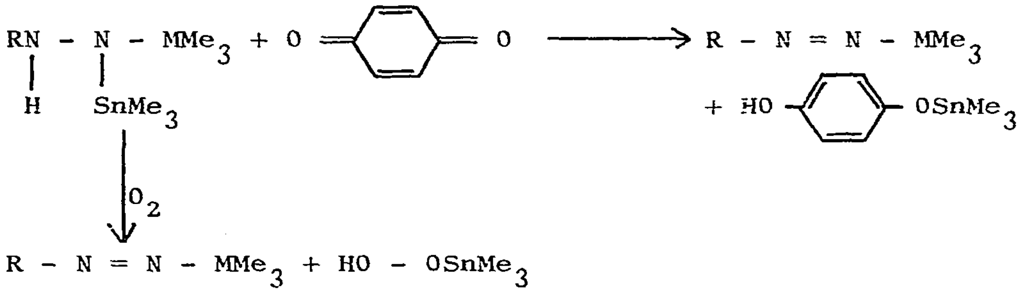


Chart 8. Synthesis of Group IVB element-substituted hydrazines.

The compounds have been shown to oxidize to substituted diimines (80):

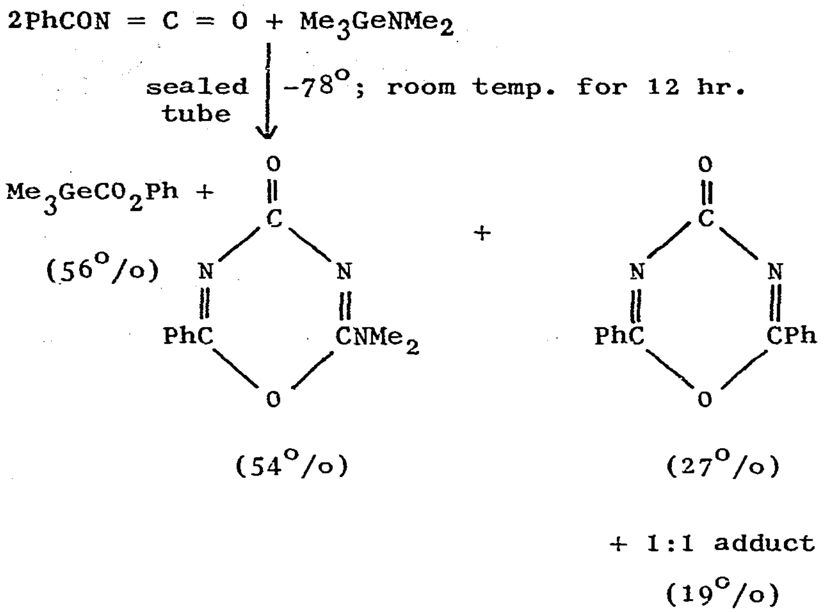


(R = t - Bu, Ph; M = Si, Ge, Sn)

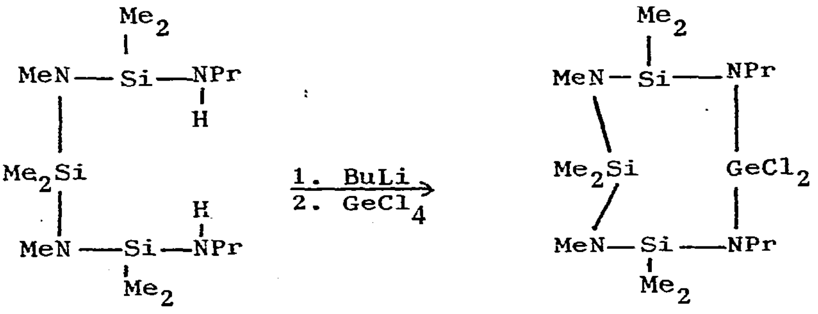
The reaction between phenyl isocyanide dichloride and Group IVB organometalloamines of the type Me_3MNMe_2 (M = Si,Ge,Sn) has been used to synthesize a variety of substituted imino compounds. The reactivity order of M has been reported to be:

Sn > Ge > Si (81):

Ishii et al. studied the insertion reactions of benzoyl isocyanate with compounds of the type Me_3MNMe_2 (M = Si,Ge,Sn) and discussed their structure (82):

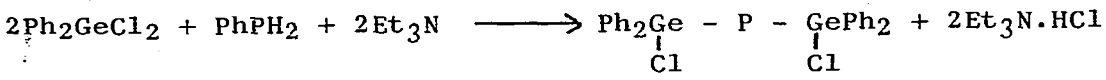


New eight-membered inorganic ring systems, containing silicon and nitrogen and also phosphorus, boron or germanium as additional ring members, have been prepared and characterized by IR and NMR (83,84):



Germanium-phosphorus compounds

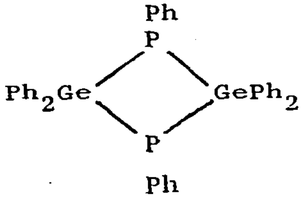
Schumann and Benda observed that whereas the reaction of diphenylgermanium dichloride and phenylphosphine in the presence of triethylamine gave only bis(diphenylchlorogermyl) phenylphosphine, analogous reaction with potassium hydrogen phenylphosphide or dipotassium phenylphosphide resulted in dimeric and trimeric (diphenylgermyl) phenylphosphine (85):



$$2Ph_2GeCl_2 + PhPH_2 + 2Et_3N \longrightarrow Ph_2\underset{Cl}{Ge}-P-\underset{Cl}{Ge}Ph_2 + 2Et_3N.HCl$$

$$nPh_2GeCl_2 + nK_2PPh \longrightarrow (Ph_2GePPh)_n + nKCl$$

(n = 2 or 3)

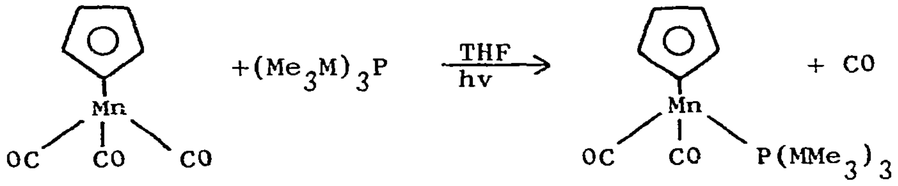


(when n = 2)

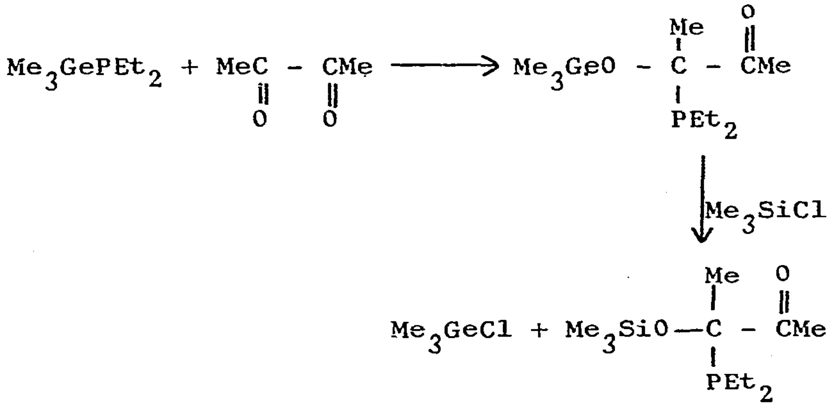
Organometal phosphine substituted transition metal complexes have been synthesized via following routes (86, 87):

$$(Me_3M)_3P + Mn(CO)_5Br \longrightarrow [(CO)_4MnP(MMe_3)_2]_2$$

(M = Ge, Sn)



Satgé et al. reported the addition of silyl- and germylphosphines to α-dicarbonyl compounds (88):



$$Me_3GePEt_2 + \underset{O}{\overset{\|}{MeC}}-\underset{O}{\overset{\|}{CMe}} \longrightarrow Me_3GeO-C(Me)(PEt_2)-C(=O)Me \xrightarrow{Me_3SiCl} Me_3GeCl + Me_3SiO-C(Me)(PEt_2)-C(=O)Me$$

Tris(triethylgermyl) stibine has been shown to associate under the influence of temperature, light and in contact with triphenylphosphine or triethylamine. The authors observed that association caused a change in the nature of the process of autooxidation from a chain free-radical (for monomeric forms) to one taking place without the participation of free-radicals (for polyassociates). The products have been shown to be (89, 90):

$$2(Et_3Ge)_2Sb + 3O_2 \longrightarrow (Et_3Ge)_2O + Sb_2O_3$$

Tris(trimethylgermyl) stibine has been used as ligand in transition metal carbonyl complexes (91):

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

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

Drake and Anderson reported the first examples of silylated and germylated polyarsines (92):

$$\begin{array}{l} (H_3Ge)_3As + Me_2AsCl \\ \qquad\qquad \Big\downarrow \text{Allowed to warm slowly from } -196 \text{ to } -78^{o} \\ Me_2AsAs(GeH_3)_2 + H_3GeCl \\ \qquad \Big\downarrow \text{room temp.} \\ Me_2AsGeH_3 + \frac{1}{n}\,(H_3GeAs)_n \end{array}$$

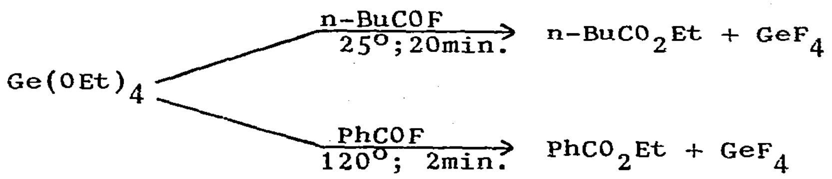
Germanium-oxygen compounds

Monomeric hexafluoroisopropoxides of silicon, germanium and titanium could be prepared via the reaction (93):

$$MCl_4 + 4(CF_3)_2CHONa \longrightarrow M[OCH(CF_3)_2]_4 + 4NaCl$$

Thermal and hydrolytic decomposition was quantitative to the oxides.

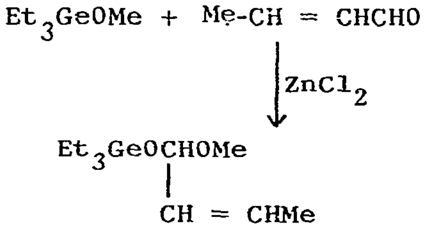
Citron synthesized various derivations of acyl fluorides according to the procedure (94):



$$Ge(OEt)_4 \xrightarrow[25^{o};\,20min.]{n\text{-}BuCOF} n\text{-}BuCO_2Et + GeF_4$$

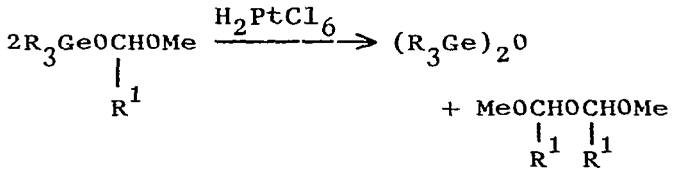
$$Ge(OEt)_4 \xrightarrow[120^{o};\,2min.]{PhCOF} PhCO_2Et + GeF_4$$

Aldehydes and ketones have been found to add onto the Ge-O bond of organogermanium alkoxides with formation of the corresponding germanium-acetals (95):



$$Et_3GeOMe + Me\text{-}CH=CHCHO \xrightarrow{ZnCl_2} Et_3GeOCH(CH=CHMe)OMe$$

In the presence of chloroplatinic acid the products have been found to decompose according to the reaction:



$$2R_3GeOCH(R^1)OMe \xrightarrow{H_2PtCl_6} (R_3Ge)_2O + MeOCH(R^1)CH(R^1)OMe$$

$(R_3 = Et_3$ or Et_2Cl; $R^1 = H$ or alkyl)

Germanium-sulfur, - selenium and - tellurium compounds

High yield synthesis of methylthio derivatives of Group IVB elements has been accomplished according to the reaction (96):

$$4RX + LiAl(SMe)_4 \longrightarrow 4RSMe + LiX + AlX_3$$

$$(80\text{-}90^{o}/o)$$

$(R = Me_3Si, Me_3Ge, Me_3Sn, GeH_3 ;\ X = Cl, Br)$

Analogous reaction with lithium tetra (methylseleno) aluminate gave the seleno derivatives in excellent yields (65-90°/o).

Compounds containing germanium-sulfur (97) and germanium-selenium (98) bond could also be prepared via the reactions:

$$\mathrm{Ph_2GeCl_2 + Pb(SC_6F_5)_2 \xrightarrow[5\text{-}15min.]{Et_2O} Ph_2Ge(SC_6F_5)_2 + PbCl_2}$$

$$\mathrm{Et_3GeOMe + n\text{-}BuSeH \xrightarrow{100^{o}} n\text{-}BuSeGeEt_3 + MeOH}$$

$$\mathrm{Et_3GeNEt_2 + n\text{-}BuSeH \xrightarrow[6hr.]{100^{o}} n\text{-}BuSeGeEt_3 + Et_2NH}$$

Vyazankin et al. reported the cleavage of chalcogen-chalcogen bond in $\mathrm{Et_2X_2}$(X = S,Te) by triethylgermyllithium thus synthesizing germanium-chalcogen derivatives (99):

$$\begin{tikzcd} \mathrm{Et_3GeLi + EtX - XEt} \arrow[r, "\mathrm{hexane}"] & \mathrm{Et_3GeXEt + EtXLi} \arrow[dl, "\mathrm{Et_3GeBr}"] \\ \mathrm{LiBr + Et_3GeXEt} & \end{tikzcd}$$

(X = S, Te)

Cleavage of the germanium-sulfur bond by electrophilic reagents has been shown to proceed according to the reaction (100):

$$\mathrm{2Bu_3GeSR + S}_m\mathrm{Cl_2} \longrightarrow \mathrm{2Bu_3GeCl + RS_{m+2}R}$$

$(\mathrm{R = p\text{-}CH_3C_6H_4,\ p\text{-}Bu^tC_6H_4;\ m = 1\ or\ 2})$

The interaction of triethylaluminum with triethylgermane selenol gave ethane and product with Ge - Se - Al grouping (101):

$$\mathrm{Et_3GeSeH{+}Et_3Al \xrightarrow[0^{o}]{hexane} [Et_3GeSeAlEt_2]_{1.7} + C_2H_6}$$

Thermal decomposition of the product was studied:

$$\mathrm{[Et_3GeSeAlEt_2]_{1.7} \longrightarrow (Et_3Ge)_2Se} + \frac{1}{n}\mathrm{(EtAlSe)_n + Et_3Al}$$

$$\mathrm{(Et_3Ge)_2Se + Et_3Al \xrightarrow{130^{o}} 2Et_4Ge} + \frac{1}{n}\mathrm{(EtAlSe)_n}$$

Alkenyl- and alkynyl-germanium compounds

One of the routes (102, 103) to synthesize alkenyl-germanium compounds has been shown to be the addition of alkoxygermanes to alkoxyacetylenes (103):

$$MeOGeX_3 + HC \equiv COR \xrightarrow{30-35^{\circ}} X_3GeCH = C(OMe)OR$$

$(X = Cl, Ph;\ R = Et, Bu)$

The reactions of unsaturated organogermanium compounds with bromine and hydrochloric acid (104) and with cyclopentadiene (105) have been studied (see Chart 9).

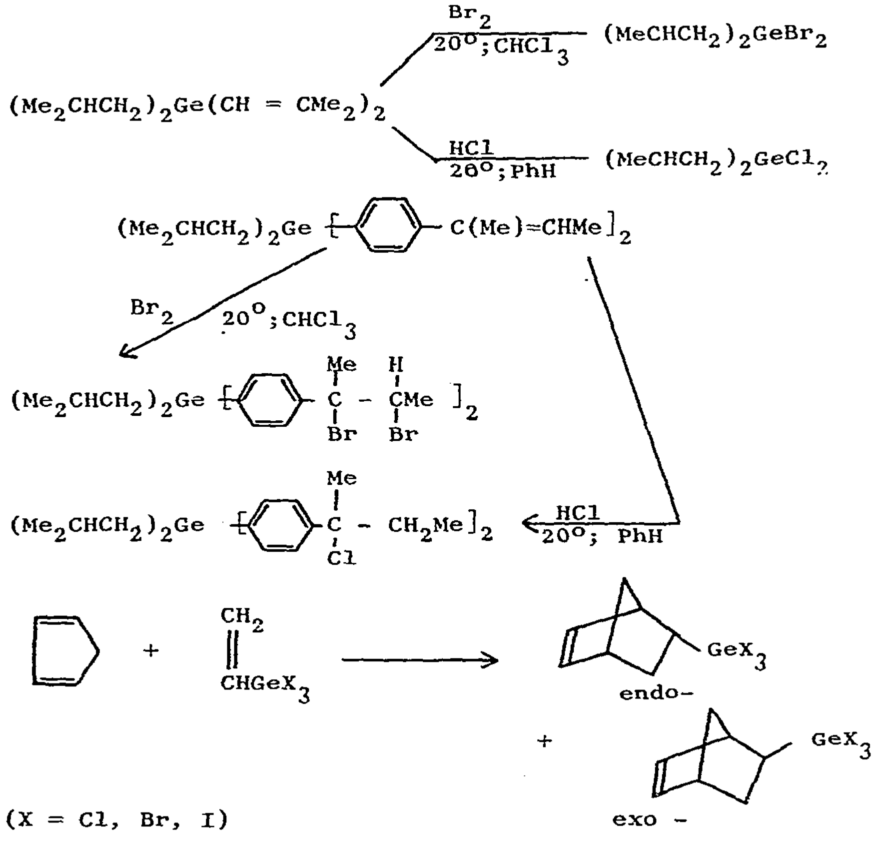
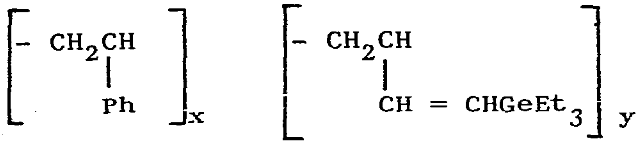


Chart 9. Reactions of unsaturated germanium compounds.

Nametkin and coworkers studied some polymerization reactions of substituted vinylgermanes (106, 107). Butadiene and isoprene were polymerized by butyllithium and vinylgermane in heptane at 20°. Degree of germanium incorporation increased in the order (106):

$Me_3GeCH = CHMe$, $Me_3GeC(Me) = CH_2$,
$Me_3GeC(Ph) = CH_2$ and $Me_3GeCH = CHPh$

The copolymerization of 1 - triethylgermyl-1,3-butadiene with styrene in the presence of 1°/o benzoyl peroxide has been shown to proceed via a 3,4-addition at the double bond to give 1-triethylgermyl - 1,3-butadiene-styrene copolymer:



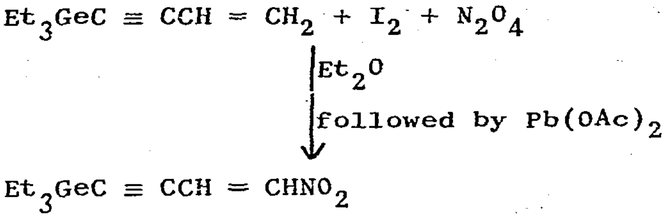
$$\left[-CH_2\underset{\displaystyle Ph}{\underset{|}{CH}}\right]_x \quad \left[-CH_2\underset{\displaystyle CH = CHGeEt_3}{\underset{|}{CH}}\right]_y$$

Structure of the copolymer was elucidated by IR spectroscopy (108).

Perfluoroalkynyl (109) and mixed-acetylenic derivatives (110) of Group IVB metals could be synthesized according to the reactions:

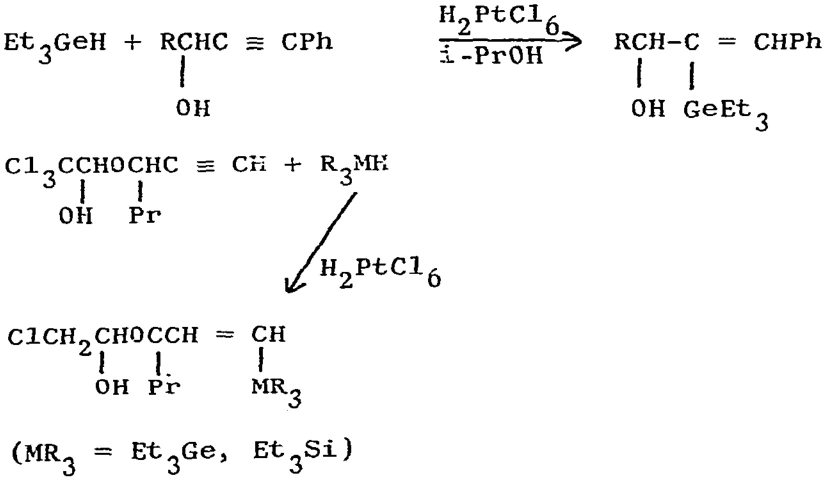
$$Me_nMX_{4-n} + RC \equiv CMgX \longrightarrow Me_nM(C \equiv CR)_{4-n}$$
$$[X = Cl, Br; R = CF_3, C_2F_5, (CF_3)_2CF]$$
$$Et_3GeC \equiv CH + Et_3SnNEt_2 \longrightarrow Et_3GeC \equiv CSnEt_3 + HNEt_2$$
$$R_3MCH_2C \equiv CH + Et_3SnNEt_2 \longrightarrow R_3MCH_2C \equiv CSnEt_3 + HNEt_2$$
$$(R = Me, Et; M = Si, Ge)$$

Petrov et al. reported first examples of silyl - and germyl nitroalkynes (111):



$$Et_3GeC \equiv CCH = CH_2 + I_2 + N_2O_4 \xrightarrow[\text{followed by } Pb(OAc)_2]{Et_2O} Et_3GeC \equiv CCH = CHNO_2$$

A number of publications regarding the addition of organohydrogermanes to alkynyl derivatives have appeared (112-115). The reactions provide convenient routes to alkenyl-germanium compounds. Some of the reactions are listed in Chart 10.



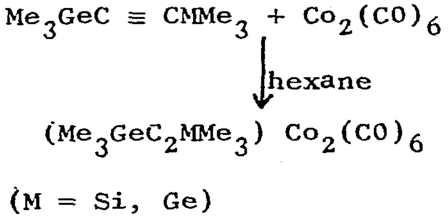
$$Et_3GeH + \underset{\displaystyle OH}{RCHC} \equiv CPh \xrightarrow[i\text{-}PrOH]{H_2PtCl_6} \underset{\displaystyle OH}{RCH}-\underset{\displaystyle GeEt_3}{C} = CHPh$$

$$Cl_3C\underset{\displaystyle OH}{CH}O\underset{\displaystyle Pr}{CH}C \equiv CH + R_3MH \xrightarrow{H_2PtCl_6} ClCH_2\underset{\displaystyle OH}{CH}O\underset{\displaystyle Pr}{C}CH = \underset{\displaystyle MR_3}{CH}$$

$(MR_3 = Et_3Ge,\ Et_3Si)$

Chart 10. Addition reactions of organohydrogermanes to alkynyl compounds.

Seyferth and White reported the dicobalt hexacarbonyl complexes of a number of Group IVB element-substituted acetylenes (116):

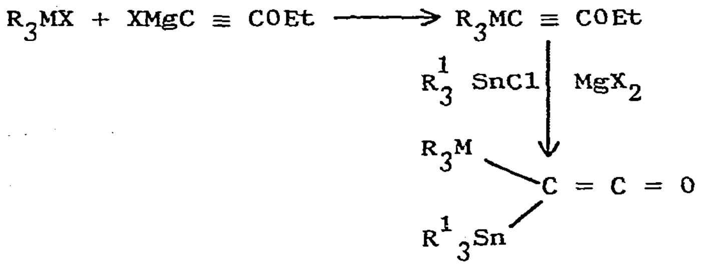


$$Me_3GeC \equiv CMMe_3 + Co_2(CO)_6 \xrightarrow{hexane} (Me_3GeC_2MMe_3)\ Co_2(CO)_6$$

$(M = Si,\ Ge)$

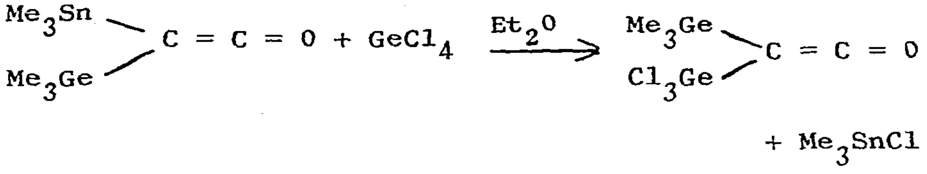
The preparation and reactions of mono - and di-metalated ketenes have been reported (117, 118):

$$R_3GeC \equiv COEt \xrightarrow{120-130^{\circ}} R_3GeCH = C = O + C_2H_4$$



$$R_3MX + XMgC \equiv COEt \longrightarrow R_3MC \equiv COEt \xrightarrow[MgX_2]{R^1_3SnCl} (R_3M)(R^1{}_3Sn)C = C = O$$

(M = Ge; R = Me, Et, R^1 = Me, Et; X = Br)

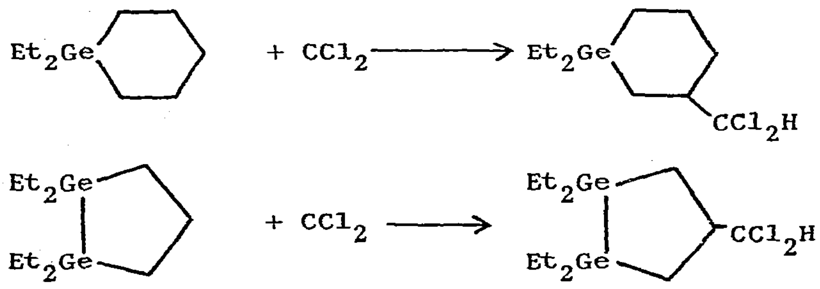


$$(Me_3Sn)(Me_3Ge)C = C = O + GeCl_4 \xrightarrow{Et_2O} (Me_3Ge)(Cl_3Ge)C = C = O + Me_3SnCl$$

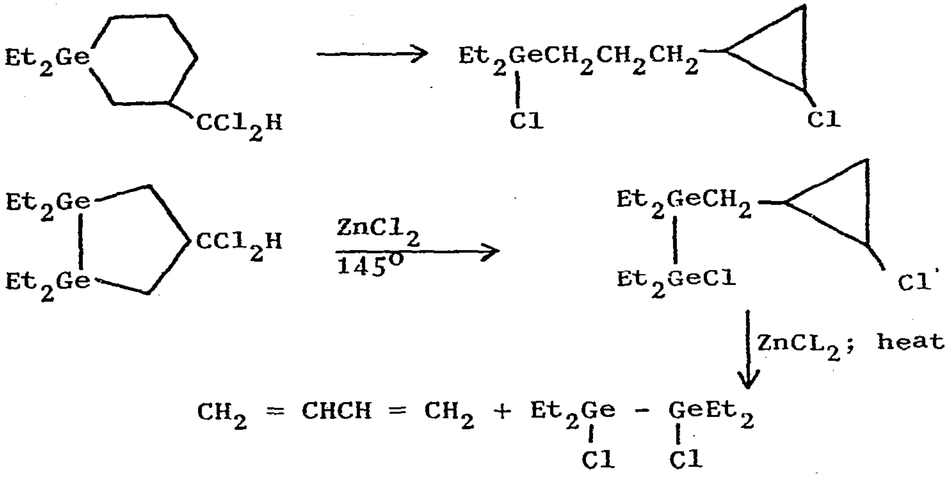
$$Et_3GeCH = C = O + Pr_3SnOMe \xrightarrow{\text{room temp.}} Et_3Ge(Pr_3Sn)CHCOOMe$$

Germacyclanes

Seyferth and coworkers studied the insertion reactions of phenyl(bromodichloromethyl) mercury derived dichlorocarbene to β C - H bonds of a number of tetraalkylgermanes and germacyclanes (119):

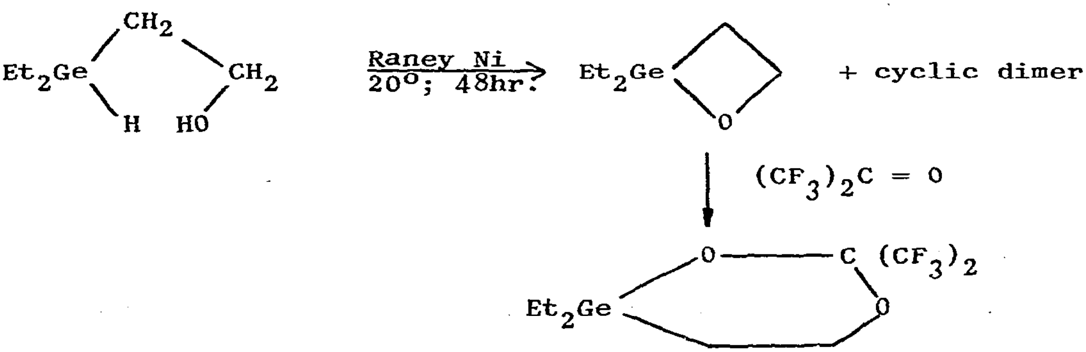


Pyrolysis of the insertion products resulted in germyl-substituted chlorocyclopropanes:

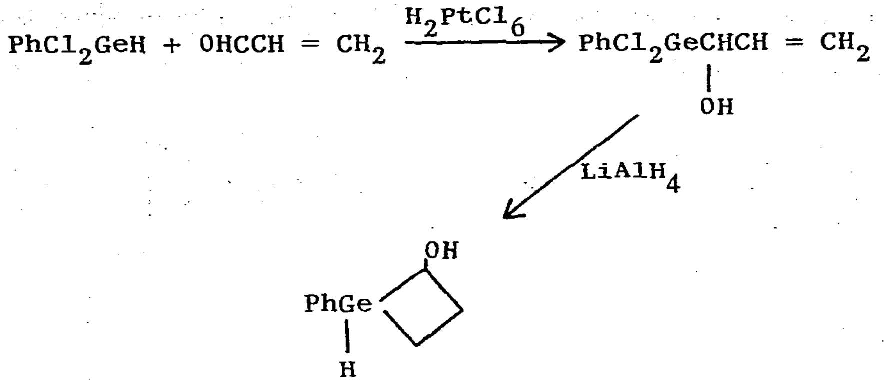


In view of the high yields with which such insertions occur in some cases, this insertion - thermolysis sequence may find useful application in synthesis.

Dehydrocondensation of β-germylated alcohols containing a Ge - H bond has been found to give germaoxetanes (120) which react with aldehydes or ketones to give corresponding dioxanes (121):



Satgé and Rivière synthesized some 1-germylallyl alcohols and studied their conversion to germacycloalkanols (122):



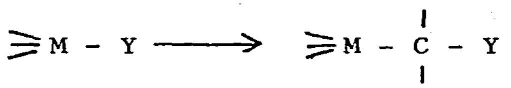
$$PhCl_2GeH + OHCCH = CH_2 \xrightarrow{H_2PtCl_6} PhCl_2GeCH(OH)CH = CH_2$$

Pyrolysis of 1,1-dimethyl - 1 - germacyclobutane has been shown to give a mixture of products e.g. 1,1,2,2-tetramethyl-1,2-digermacyclopentane, cyclopropane, ethylene etc. [detected by gas-chromatography and IR spectra (123)].

Zuckerman and Yoder reviewed the preparation and reactions of heterocyclic compounds of Group IVB elements (124). The preparation of 1-germa-3-sila(germa)-cyclobutanes has been patented (125).

Carbon-functional germanium compounds

The reactions involving the introduction of a methylene bridge (CH_2, CHX, CX_2 etc.) into a Group IVB element-to-other element covalent bond:



$$\geqslant M - Y \longrightarrow \geqslant M - \overset{|}{\underset{|}{C}} - Y$$

(M = Si, Ge, Sn, Pb; X = H, Hg, halogen etc.)

have been reviewed (126). Reagents which effect such methylenation include diazoalkanes carbenes and 'carbenoid' organometallics. The reaction of trimethylchlorogermane with iodomethylzinc iodide has been found to give $Me_3GeCH_2I(2^o/o)$ and $(Me_3Ge)_2CH_2(7^o/o)$. Formation of the methylene-bridged digermane has been explained in terms of a halogen metal exchange-alkylation sequence (127):

$$Me_3GeCH_2I + ICH_2ZnI \longrightarrow Me_3GeCH_2ZnI + CH_2I_2$$

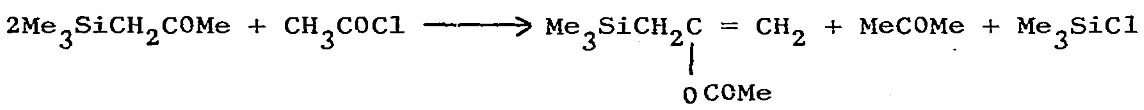
$$Me_3GeCH_2I + Me_3GeCl \longrightarrow Me_3GeCH_2GeMe_3 + ZnClI$$

Better yields of Me_3GeCH_2I could be obtained via the reaction scheme:

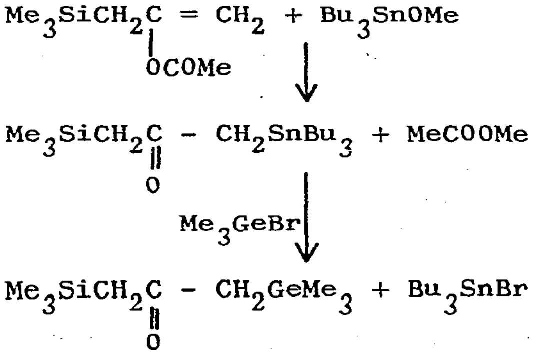
$$\begin{tikzcd} GeCl_4 + ICH_2ZnI \arrow[r] & Cl_3GeCH_2I \arrow[d, "\begin{array}{c}THF/(Me_2N)_3PO\\ 9/1\end{array}"', "MeMgBr"] \\ & \begin{array}{cc} Me_3GeCH_2I & + (Me_3Ge)_2CH_2 \\ (29^{o}/o) & (trace) \end{array} \end{tikzcd}$$

Several publications regarding synthesis of a variety of carbon-functional germanium compounds have appeared (128-138). Some of these are compiled in Chart 11.

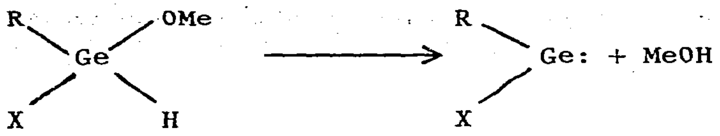
$$2Me_3GeNMe_2 + CH_2N_2 \xrightarrow{Et_2O} (Me_3Ge)_2CN_2 + 2HNMe_2$$



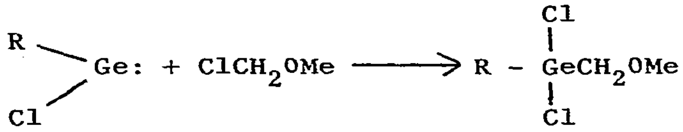
$$2Me_3SiCH_2COMe + CH_3COCl \longrightarrow Me_3SiCH_2\underset{OCOMe}{\underset{|}{C}} = CH_2 + MeCOMe + Me_3SiCl$$



$$\begin{tikzcd} Me_3SiCH_2\underset{OCOMe}{\underset{|}{C}} = CH_2 + Bu_3SnOMe \arrow[d] \\ Me_3SiCH_2\underset{O}{\underset{\|}{C}} - CH_2SnBu_3 + MeCOOMe \arrow[d, "Me_3GeBr"'] \\ Me_3SiCH_2\underset{O}{\underset{\|}{C}} - CH_2GeMe_3 + Bu_3SnBr \end{tikzcd}$$

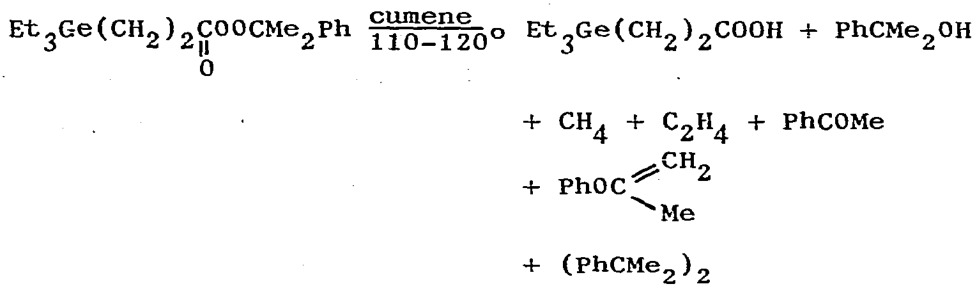


(R = Et, Ph; X = F, Cl, Br, I)



(R = Cl, Et, Ph)

Thermal decomposition of cumyl esters of β-(triethylgermyl) propionic acids has been reported to yield complex mixtures of products (139):



$$Et_3Ge(CH_2)_2\underset{\|\atop O}{C}OOCMe_2Ph \xrightarrow[110-120^\circ]{cumene} Et_3Ge(CH_2)_2COOH + PhCMe_2OH + CH_4 + C_2H_4 + PhCOMe + PhOC(=CH_2)Me + (PhCMe_2)_2$$

Redistribution reactions

Redistribution reactions including those of germanium compounds have been reviewed (140). Synthesis of a number of organohologermanium hydrides has been accomplished via redistribution reactions of the type (141):

$$RGeCl_3 + MeSiHCl_2 \xrightarrow{AlCl_3} RGeHCl_2 + MeSiCl_3$$

(R = Me, Et, i-Bu)

Products were characterized by IR-, NMR-spectroscopy and glpc. The method, apart from its simplicity, has the advantage of starting from cheaper and readily available silicon compounds.

Physico-chemical investigations

The relative basicities of a number of compounds containing M - N or M - O (M = Si, Ge) bonds have been determined (142-145). On the basis of these results it has been concluded that a more significant (p - d)π bonding takes place in Ge - N bond than in Ge - O bond. Jolly explained the decrease in the acidity of germane and the phenylgermanes with increasing phenyl substitution in terms of two opposing effects of phenyl substitution: an acid weakening effect (which is ascribed to $p_\pi - d_\pi$ bonding) and an acid strengthening effect (mainly due to $p_\pi - p_\pi$ bonding) (146). The acidity (studied by IR spectroscopy) of hydroperoxides of the type Ph_3MOOH(M = C, Si, Ge, Sn) has been found to decrease in the order: Si > Ge > Sn. The results have been explained in terms of $d_\pi - p_\pi$ conjugation (147).

The dipole moments of alkoxy germanes, $R^1{}_nGe(OR)_{4-n}$ (R^1 = Me, Pr; R = Et, Pr, t-Bu), have been shown to decrease with increasing steric volume of the alkoxy group (148). According to Bellama et al. the trends of the dipole moments of X_3GeH(X = Cl, Br, I) derivatives parallel those of methyl rather than silyl compounds (149).

A study of the hydrolysis of Me_3MCl and Me_3MOEt (M = C, Si,Ge, Sn) type compounds indicated the rates to fall as M changes in the order:

Si > Ge > Sn > C [for Me_3MCl (150)] and
Sn > Ge > Si > C [for Me_3MOEt (151)].

The rate of cleavage of $XC_6H_4(C \equiv C)_nMEt_3$ compounds (n = 2, 3; M = Si, Ge) by aqueous-methanolic alkali at 29.6°

indicated the germanium compounds to be less reactive than the corresponding silicon compounds and also less sensitive to changes in X. For a given set of $Ph(C \equiv C)_nMEt_3$ compounds the ease of cleavage increases with the change in n from 1 to 2 to 3. The effect, which is attributed to the inductive withdrawal of electrons by the additional alkynyl groups is particularly marked for the change from n = 1 to n = 2 (152). Alkaline cleavage of carbon-metal bond in Group IVB organometallics has been reviewed in terms of $S_E1(N)$ mechanism (153). The kinetic dats for the reaction:

$$Ph_3MMn(CO)_5 + L \xrightarrow[150-190^o]{decalin} Ph_3MMn(CO)_4L$$

(M = Ge, Sn; L = Ph_3P, Bu_3P)

suggest two competing mechanisms in which the rate-determining steps involve slow fission of Mn-CO bonds, and nucleophilic attack of L on the substrate (154).

Kinetic data for the reaction of compounds of the type Et_4M (M = Si, Ge, Sn, Pb) with ozone (155), iodine cleavage of Group IVB hexaalkyldimetals (156) and the reaction of Me_3MCl and Me_2MCl_2 (M = Ge, Sn) with sodium (157) have been reported.

Stereochemistry of main Group IV elements (including organogermanium compounds) has been discussed (158). The compounds containing an asymmetric carbon directly bonded to the metal atom could be synthesized via the reaction (159):

$$\begin{array}{c} Ph_3MBr + Na + NH_3 + (S) - (+) - sec - BuBr \\ \downarrow \\ (R) - (-) - sec - BuMPh_3 \end{array}$$

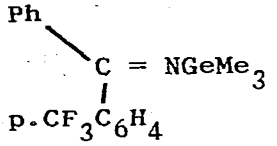
(M = Si, Ge, Sn, Pb)

A chiral germyl radical produced from an optically active hydrogermane has been shown to abstract a chlorine atom from carbon tetrachloride to give corresponding chlorogermane with retention of configuration (160):

$$R_3Ge^{*} + CCl_4 \xrightarrow[\text{peroxide}]{\text{dibenzoyl}} R_3Ge^{*}Cl$$

(R = 1-NpPhMe)

The heats of combustion of some tetraalkylgermanes (161) and of tetraorganooxygermanes (162) have been reported. The results of thermal decomposition of tetraalkylgermanes indicated that with increase in the length of the alkyl chain the extent of β-breakdown into hydrogen and olefin increases (163,164). The saturated vapour pressures of a number of organolhalogermanes have been measured by static and dynamic methods (165). The photolysis of Ph_3Ge-COPh (166) and the vacuum-ultraviolet photolysis of H_3GeCl(167) gave free radical species of the type Ph_3Ge and H_2ClGe respectively. Force constants have been calculated for compounds of the type X_3GeH(X = F,Cl,Br,I) and verified by calculation of vibrational frequencies for Cl_3GeD(168). According to Seip the barriers to pseudorotation in silacyclopentane and germacyclopentane calculated with the Westheimer - Hendrickson method, agree reasonably well with the reported experimental values (169). Pyramidal inversion energy barriers in $RPhPMMe_3$ (R = Me or i-Pr; M = C,Si,Ge,Sn) compounds decreased linearly with the electronegativity values of the heteroatoms (M) and with chemical shifts of the protons in methyl groups attached to M(170). The first experimental demonstration of a similar effect on the barrier to planar nitrogen inversion for the compound



$$\mathrm{Ph(p\text{-}CF_3C_6H_4)C = NGeMe_3}$$

has been reported (171).

Seyferth and White reported the rearrangement of o-bis (trimethylsilyl) benzene to its m(93^{o}/o) and p(5^{o}/o) isomers at 150^{o} in benzene in a sealed tube in the presence of 2.5 mole ^{o}/o of CF_3COOH (172). Analogous experiments with o-bis(trimethylgermyl) benzene showed no rearrangement. The explanation for this probably lies in the fact that the acid catalyst is consumed in germanium-carbon bond protolysis at a faster rate than that of the rearrangement of the o-isomer.

Some other studies include: electroreduction of R_3MX and R_2MX_2 (R = Et, Bu, Ph; M = Si, Ge, Sn; X = Cl, Br) compounds (173); solubilities of R_4M (R = alkyl; M = C, Si, Ge, Sn) compounds (174); calculation of approximate force field of germylacetylene (175); electron bombardment of SiH_4 and GeH_4 (176); molecular association of Gr.IV element tetrachlorides in cyclohexane (degree of association for $GeCl_4$ = 1.6)(177); molecular orbital calculations of the electronic structure of fluorogermane (178); $\sigma - \pi$ conjugation of carbon-metal bonds (179); fluxional behaviour of some organometallic compounds (including those of germanium) (180); mechanism of the reaction of germylpotassium with organic halides (181) and electronegativity and π-bonding effects on bond strengths of silicon and germanium (182).

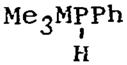
Spectral studies

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

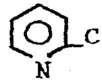
IR and Raman studies

The far-infrared and low frequency Raman spectra of solid $EtSiH_3$, $EtSiD_3$, $EtGeH_3$ and $EtGeCl_3$ have been recorded (183). The data indicated a gradual decrease in the barrier to the internal rotation of the methyl group as one goes from propane to ethylsilane to ethylgermane. Fontal and Sprio reported a staggered D_{3d} configuration for hexamethyldigermane on the basis of Raman and IR frequencies assigned to the various skeleton modes of the hexamethyldimetal derivatives of Group IVB elements (184). More specific studies include the following compounds:
MX_4 (M = C, Si, Ge, Sn, Pb , X = Cl, Br, I) (185-187);
GeH_3^- (188); $MeGeHX_2$ (X = F, Cl, Br, I) (189);
Me_nGeI_{4-n} (n = 1, 2 or 3) (190); $MeGeI_3$ and CD_3GeI_3 (191);
R_3GeOR and $R_3GeOGeR_3$ (R = alkyl) (192); $CH_2 = CHGeH_3$ (193);
$CH_2 = CHGeCl_3$ (194); $Me_nM(C \equiv CR)_{4-n}$ [M = Si, Ge, Sn; n = 0-3;
R = CF_3, C_2F_5, $(CF_3)_2CF$] (109); eight-membered inorganic ring systems containing Si, Ge and N(84); $(H_3Ge)_2Fe(CO)_4$(195); Ph_3M
$[Fe(CO)_2L(NO)]$ [M = Ge, Sn; L = CO or $P(OPh)_3$] (64);
$(Me_3M)_3SbM^1(CO)_5$ (M = Ge, Sn; M^1 = Cr, Mo, W)(91); $(\pi - C_5H_5)(CO)_3$
$M^1M^2Me_3$ (M^1 = Cr, Mo or W; M^2 = Ge or Sn)(196); $(Me_3GeC_2MMe_3)$
$Co_2(CO)_6$ (M = Si, Ge) (116); $[(CO)_4MnP(MMe_3)_2]_2$ (M = Ge,Sn) (86)
and $Me_3MRu(CO)_4$ X (M = Si, Ge; X = Br, I) (67).

NMR studies

Kakhniashvili and Ioramashvili investigated the addition reactions of trialkylhydrogermanes to vinylalkynyl systems in the presence of chloroplatinic acid as catalyst (197, 198), using NMR spectroscopy. Free radical addition of thiols to 1,3-diynic germa hydrocarbons has been shown (by NMR spectroscopy) to take place at both the triple bonds forming a complex mixture of enynic sulfides (199). Other studies and articles include: PMR studies of the self-exchange of $(Me_3Ge)_2Hg$ (200); some exchange reactions of halomethylgermanes (201); the exchange equilibrium of the substituents Cl, Br, I and PhO between Me_2Si and MeGe moities and between MeSi and Me_2Ge moities (202); thermal rearrangement of trialkylgermanium acetic acid amides into N-trialkylgermanium acetamides (203); proton chemical shifts and spin-spin coupling constants for compounds of the type $Me_3MM^1Me_3$ (M & M^1 = C, Si, Ge, Sn) (204); ^{14}N - NMR chemical shifts of some Group IVB isothiocyanates (205); ^{13}C - chemical shifts and PMR data of numerous acetylenic derivatives including those of germanium (206); NMR spectra of  $Me_3M\underset{H}{P}Ph$ (M = Si, Ge, Sn) compounds (207); methyl chemical shifts and ^{13}C - H coupling constants for aryltrimethylgermanes (208); temperature dependence of the NMR spectra of $(C_5H_5)_2GeH_2$ (209) and $(C_5H_5)_2Ge[Fe(CO)_2C_5H_5 - \pi]_2$ (210); NMR spectra of germylated sulfur ylids (211); NMR data for 9 - germa - dihydroanthracenes (212); NMR spectra of complexes of the type $Ph_3GeFe(C_4H_6)(C_5H_5)$ (213) and the study indicating that the proton spin-rotation constants in SiH_4 and GeH_4 are positive and the ^{19}F spin-rotation constants in CF_4, SiF_4 and GeF_4 are negative (214).

<u>Miscellaneous</u>

The results of the UV spectra of $PhCH_2GeMe_3$ (215) and  CH_2MMe_3 (M = C, Si, Ge, Sn)(216) have been explained in terms of σ - π conjugation.

Kenworthy and Myatt extended their study on the ESR spectra of the frozen solutions of complexes of titanocence (217). The ESR spectrum of a series of alkyl radicals heterosubstituted in the β-position with S, Si, Ge, Sn has been investigated (218).

Wallbridge and Fishwick (219) observed that the fragmentation patterns of the tetraallyl derivatives of the Group IVB elements, $M(C_3H_5)_4$ (M = Si, Ge, Sn), sharply depend on the central atom, and are related to the stability of the M-C bond. The most abundant species in the mass spectra of $Me_3M - M^1Me_3$ and Me_4M (M and M^1 = C, Si, Ge, Sn, Pb) compounds has been shown to be the ion $C_3H_9M^+$(220, 221). Vapour-phase bimolecular reactions of alkyl siliconium and other metal ions in mass spectrometry (222) and the mass spectroscopic study of Group IVB acetylides (223) have been reported.

A number of publications on photoelectron spectra of Group IVB halides have appeared (224-227). Maslowsky surveyed the vibrational spectra of intra - and inter-metal bonds (228). The complete absorption spectra for compounds of the type $X_3MCo(CO)_4$ (M = Si, Ge, X = Cl, Br, I) indicated the metal-metal bond being σ in character and that although the π character of the M-M bond is relatively small, the Co - Sn bond has more π character than the Co-Ge bond (229). Preliminary attempts regarding spectroscopic observation of silane and germane decomposition products under a variety of conditions in a flow system has been studied in view of the elucidation of the mechanisms of several synthetically useful and mechanistically interesting reactions (230). The vibrational spectra for trimethylgermanium nitrate (231) and dimethyl-germanium dinitrate (232) have been reported. The nitrato groups are covalently bound to germanium atom in a unidentate manner.

The reports regarding structural data for various organo-germanium compounds include:structure of tribromogermylmanganese pentacarbonyl in gas-phase by electron diffraction (233); crystal structure of 1-(α-naphthyl) germatrane (234); crystal and molecular structure of trigerma-s-triazine, $(Cl_2GeNMe)_3$(236); crystal structure of tris-μ-(dimethylgermanio)-tris (tricarbonylruthenium) (235) (Fig. 1); crystal structure of tetraphenylgermane (237) (Fig.2) and crystal structure of cis-(hydroxydiphenylgermyl)

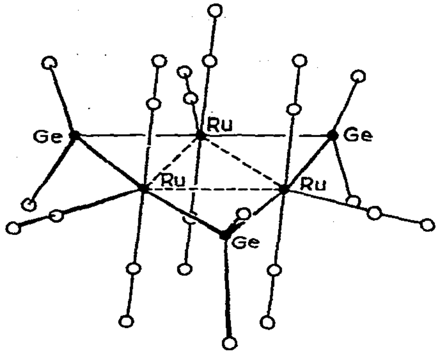


Fig. 1. Perspective view of $[Ru(CO)_3(GeMe_2)]_3$ (from J.Howard and P. Woodward; J.Chem.Soc.A, (1971) 3648)

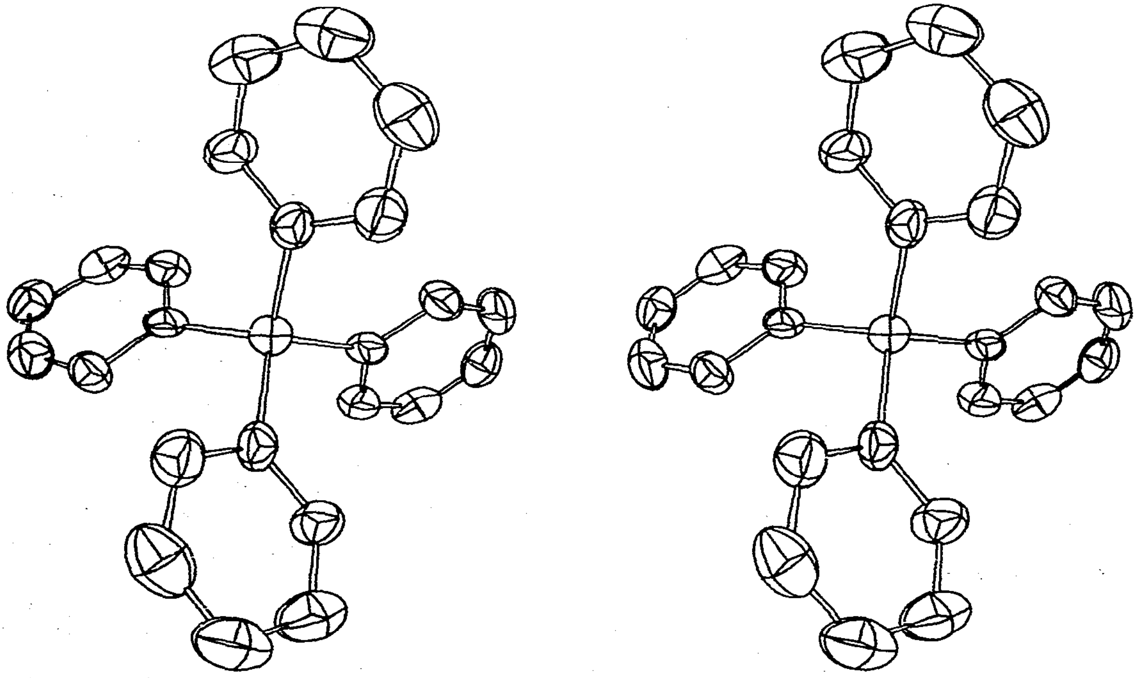


Fig. 2. The structure of tetraphenylgermane (from P.C. Chieh; J. Chem. Soc. A, (1971) 3243)

phenylbis (triethylphosphine) platinum (II) (238).

Analysis, applications and biological effects

A modified method for the determination of germanium, carbon and hydrogen in organogermanium compounds has been reported (239).

Vyazankin et al. studied the possible separation of a number of organogermanium compounds by gas chromatography (240 - 242).

A number of claims have been made for the use of organogermanium compounds as PVC-stabilizers (243-245). Other claims include: photconductive layers containing organogermanium compounds (246); organogermanium compounds in hydrolysis-proof coatings (247); mesomorphic substances containing Group IVB elements (248); organogermanium compounds in the treatment of cancer cells (249) and addition reactions of the Group IVB organometallic compounds and their synthetic applications (250).

The toxicity of organometallic compounds of the type R_3MX (R = Me, Et, Pr; X = AcO, OH, Cl; M = Si, Ge, Sn, Pb) to aquatic organisms (251) and effect of $(Bu_3Ge)_2O$ on the inhibition of respiration (252) in certain types of cells have been reported.

REFERENCES

1. M.Lesbre, P.Mazerolles and J.Satgé; "The Organic Compounds of Germanium", John Wiley & Sons, London, 1971.
2. E.Becker and M.Tsutsui (Editors); "Organometallic Reactions", Vol. 1 & 2, Wiley-Interscience, New York, 1971.
3. M.Lesbre; Bull.Union Physiciens, 65 (1970)1; Chem.Abstr.,74 (1971) 112079s.
4. W.P. Neumann; Pure Appl.Chem., 23 (1970) 433; Chem.Abstr., 74 (1971) 112086s.
5. F.G.A. Stone; U.S.Clearinghouse Fed.Sci.Tech.Inform., AD(1970) 714623; Chem.Abstr., 75(1971) 20455d.
6. R.A. Jackson; Chem.Soc.Spec.Publ.No.24 (1971) 295.

7. D.J. Cardin, M.F.Lappert, J.D. Smith and D.R.M. Walton; Annu.Rep.Progr.Chem.B, (1970) 271.

8. D.W.A. Sharp, M.G.H. Wallbridge and J.H.Holloway; Annu.Rep. Progr.Chem. A, (1970) 255.

9. N.V. Fomina, V.V. Pondeev, N.I.Sheverdina and K.A.Kocheshkov; Dokl.Akad.Nauk SSSR, 194 (1970) 1344; Chem.Abstr., 74 (1971) 100175g.

10. G.Ya. Zueva, N.V. Luk'yankina and V.A. Ponomarenko; USSR Pat. 276, 956; Chem.Abstr., 74 (1971) 64309t.

11. V.F. Mironov, L.M. Kalinina, E.M.Berliner and T.K. Gar; Zh.Obshch.Khim., 40 (1970)2597; Chem.Abstr., 75 (1971) 49255z.

12. M. Massol, J. Barrau and J. Satgé; Inorg.Nucl.Chem.Lett., 7(1971) 895.

13. T.L. Tursunbaev, Z.M. Manulkin and A.N.Tatarenko; Zh.Obshch. Khim., 40 (1970) 1300; Chem.Abstr., 74 (1971) 53943u.

14. I.I. Lapkin, V.A. Dumler and E.S. Ponosova; Zh.Obshch.Khim., 41 (1971) 133; Chem.Abstr., 75 (1971) 20546j.

15. I.M. Gverdtsiteli, M.M. Menteshashvili and T.P. Doksopulo; Zh. Obshch.Khim., 40 (1970) 1766; Chem.Abstr. 74 (1971)100178k.

16. Ya.G.Zueva, N.V. Luk'yankina and V.A.Ponomarenko; Izv.Akad. Nauk SSSR, Ser.Khim., (1971) 656; Chem.Abstr., 75 (1971)49256a.

17. L.M. Pribytkova, A.V.Kisin, Yu.N.Luzikov, N.P.Makoveyeva, V.N. Torochesshnikov and Yu.A.Ustynyuk; J.Organometal. Chem., 30, (1971) C57.

18. B.D. Jones; Rec.Chem.Progr., 31 (1970) 199; Chem.Abstr., 74 (1971) 93857a.

19. C.H. Van Dyke; Prep.Inorg.React., 6 (1971) 157; Chem.Abstr., 75 (1971) 125941n.

20. C.J. McCormick; Diss.Abstr.Int.B, 31 (1970) 3242; Chem.Abstr., 75 (1971) 76972n.

21. F.E.J. Kennedy; Diss.Abstr.Int.B, 31(1971) 5862; Chem.Abstr., 75 (1971) 76974q.

22. W.L. Jolly, T. Birchall and D.S. Rustad; US Pat. 3,535, 355; Chem.Abstr., 74 (1971) 42493w.

23. J.E. Bentham, S. Cradock and E.A.V. Ebsworth; Inorg.Nucl. Chem.Lett., 7 (1971) 1077.

24. O.V.Kuz'min, N.S.Nametkin, T.I.Chernysheva, T.K.Gar, N.A. Lepetukhina and V.F. Mironov; Dokl.Akad.Nauk SSSR, 193 (1970) 826; Chem.Abstr., 74 (1971) 31819f.

25. T.K. Gar, E.M.Berliner and V.F.Mironov; Zh.Obshch.Khim., 41 (1971) 348; Chem.Abstr., 75 (1971) 36264b.

26. V.F.Mironov, E.M. Berliner and T.K. Gar; USSR Pat. 300, 469; Chem.Abstr., 75 (1971) 63980p.

27. T.K. Gar, E.M.Berliner, A.V.Kisin and V.F. Mironov; Zh.Obshch. Khim., 40(1970) 2601.

28. G.K. Barker and J.E. Drake; Inorg.Nucl.Chem.Lett., 7 (1971) 39.

29. J.M. Bellama and C.J. McCormick; Inorg.Nucl.Chem.Lett., 7 (1971) 533.

30. C.H. Van Dyke, J.E. Bulkowski and N.Viswanathan; Inorg.Nucl. Chem. Lett., 7 (1971) 1057.

31. F.Fehér and P.Plichta; Inorg.Chem., 10 (1971) 609.

32. W.A. Ledoux and R.N. Grimes; J.Organometal. Chem., 28 (1971) 37.

33. K.I. Kobrakov, T.I.Chernysheva and N.S.Naketkin; Dokl.Akad. Nauk SSSR,198 (1971) 1340; Chem.Abstr., 75 (1971) 129908e.

34. T.K. Gar, A.A.Buyakov, A.V.Kisin and V.F.Mironov; Zh.Obshch. Khim., 41 (1971) 1589; Chem.Abstr., 75 (1971) 129212y.

35. N.S.Vyazankin, G.A. Razuvaev and O.A. Kruglaya; Z.Chem., 11 (1971) 53.

36. V.T. Bychkov, N.S. Vyazankin and G.A. Razuvaev; Zh.Obshch. Khim., 41 (1971) 716; Chem.Abstr., 75 (1971) 36285j.

37. N.S.Vyazankin, V.T.Bychkov, O.V. Linzina, L.V.Aleksandrova and G.A.Razuvaev; J.Organometal Chem.31 (1971) 311.

38. G.S. Kalinina, B.I.Petrov, O.A.Kruglaya and N.S.Vyazankin; Izv.Akad.Nauk, SSSR, Ser.Khim., (1970) 2158; Chem.Abstr. 74 (1971) 42449m.

39. E.N.Gladyshev, N.S.Vyazankin, V.S.Andreevichev, A.A.Klimov and G.A. Razuvaev; J.Organometal.Chem., 28 (1971) C42.

40. M.N.Bochkarev, L.P.Maiorova, A.I.Charov and N.S.Vyazankin; Zh.Obshch.Khim., 41 (1971) 1408.

41. S.W. Bennett, C. Eaborn, R.A. Jackson and R. Pearce; J. Organometal.Chem., 28 (1971) 59.

42. S.W. Bennett, C. Eaborn, R.A. Jackson and R.W. Walsingham; J. Organometal Chem., 27 (1971) 195.

43. V.N. Glushakova and Yu.A.Aleksandrov; Zh.Obshch.Khim. 41 (1971) 1751.

44. O.A. Kruglaya, B.I. Petrov and N.S. Vyazankin; Izv.Akad. Nauk SSSR, Ser.Khim., (1970) 2413; Chem.Abstr., 75 (1971) 49253x.

45. N.S. Vyazankin, O.A. Kruglaya, B.I. Petrov, A.N.Egorochkin and S.Ya.Khorshev; Zh.Obshch.Kim. 40 (1970) 1279; Chem.Abstr., 74 (1971) 53958c.

46. B.I.Petrov, V.R.Polishehuk, L.S.German, O.A. Kruglaya and N.S. Vyazankin; Dokl.Akad.Nauk SSSR, 193 (1970) 1315, Chem.Abstr., 74 (1971) 31824d.

47. O.A. Kruglaya, Yu.I.Baukov, B.I.Petrov and N.S.Vyazankin; Zh.Obshch.Khim., 41(1971) 1408.

48. E.J. Bulten and J.G. Noltes; J. Organometal Chem., 29 (1971) 397.

49. E.J. Bulten and J.G. Noltes; J.Organometal,Chem., 29 (1971) 409.

50. D.J. Sandman and R. West; J.Organometal.Chem. 30 (1971) C61.

51. C.F. Shaw and A.L. Allred; Inorg.Chem.,10 (1971) 1340.

52. F.C. Shaw; Diss.Abstr.Int.B., 31 (1971) 5865; Chem.Abstr., 75 (1971) 70814r.

53. C.G. Savory and M.G.H. Wallbridge; J.Chem.Soc.D., (1971) 622.

54. P.S. Braterman; Annu.Rep.Progr.Chem. A, (1970) 391.

55. H. Burger and H.J. Neese; J. Organometal.Chem. 32 (1971) 223.

56. S.A. Keppie and M.F. Lappert; J.Chem.Soc.A., (1971) 3216.

57. E.N. Gladyshev, N.S.Vyazankin, Yu.A. Sorokin, V.I. Ermolaev, G.N. Bortnikov and G.A. Razuvaev; Dokl.Akad.Nauk SSSR, 194 (1970) 1083; Chem.Abstr., 74 (1971) 42461j.

58. T.J. Marks and A.M. Seyam; J. Organometal.Chem., 31 (1971)C62.

59. H. Schumann, O. Stelzer, J.Kuhlmey and U.Niederreuther; Chem.Ber., 104 (1971) 993.

60. T.J. Marks; J. Amer.Chem.Soc., 93 (1971) 7090.

61. J.K. Ruff; Inorg. Chem., 10 (1971) 409.

62. A.J. Cleland, S.A. Fieldhouse, B.H. Freeland and R.J.O'Brien; J.Chem.Soc.D, (1971) 155.

63. H.C. Clark and B.K. Hunter; J. Organometal Chem., 31(1971) 227.

64. A.J. Cleland, S.A. Fieldhouse, B.H. Freeland, C.D.M.Mann and R.J. O'Brien; J.Chem.Soc.A., (1971) 736.

65. M. Casey and A.R. Manning; J.Chem.Soc.A., (1971) 256.

66. S.A.R. Knox and F.G.A. Stone; J.Chem.Soc.A., (1971) 2874.

67. M.J. Ash, A. Brooks, S.A.R. Knox and F.G.A. Stone; J.Chem. Soc. A, (1971) 458.

68. N.S. Vyazankin, G.S. Kalinina, V.I. Ermolaev and Yu.A. Sorokin; Zh.Obshch.Khim., 40 (1970) 1757; Chem.Abstr. 74 (1971) 31818e.

69. K. Ogino and T.L. Brown; Inorg.Chem. 10 (1971) 517.

70. A.J. Cleland, S.A. Fieldhouse, B.H. Freeland and R.J. O'Brien; J.Organometal.Chem. 32(1971) C15.

71. F. Glockling and G.C. Hill; J.Chem.Soc.A, (1971) 2137.

72. W.A.G. Graham and A.J. Oliver; Inorg.Chem., 10 (1971) 1.

73. K.A. Hooton; J.Chem.Soc.A, (1971) 1251.

74. V.I. Ermolaev, Yu.A. Sorokin, E.N. Gladyshev, N.S. Vyazankin and G.A. Razuvaev; Zh.Obshsch.Khim., 41(1971) 1878; Chem.Abstr. 75 (1971) 151879t.

75. U. Belluco, G. Deganello, R. Pietropaolo and P. Uguagliati; Inorg.Chim.Acta, Rev., 4(1970)7.

76. J.E. Bentham, S.Cradock and E.A.V. Ebsworth; J.Chem.Soc.A, (1971) 587.

77. J.E. Bentham and E.A.V. Ebsworth; J.Chem.Soc.A, (1971) 2091.

78. A.F. Clemmit and F. Glockling; J.Chem.Soc.A, (1971) 1164.

79. N. Wiberg and M. Veith; Chem.Ber., 104 (1971) 3176.

80. N. Wiberg and M.Veith; Chem.Ber., 104 (1971) 3191.

81. K. Itoh, A. Nozawa and Y. Ishii; Organometal.Chem.Syn., 1 (1970) 23.

82. K. Itoh, I. Matsuda and Y. Ishii; J.Chem.Soc. C, (1971) 1870.

83. F. Rabet and U. Wannagat; Z.Anorg.Allg.Chem., 384 (1971) 115.

84. U. Wannagat and L. Gerschler; Z.Anorg. Allg.Chem., 383 (1971) 249.

85. H. Schumann and H. Benda; Chem.Ber., 104 (1971) 333.

86. H. Schumann and H.J. Kroth; J. Organometal. Chem.,32 (19171) C47.

87. H. Schumann, O. Stelzer, J.Kuhlmey and U.Niederreuther; J. Organometal. Chem., 28 (1971) 105.

88. J. Satgé, C.Couret and J.Escudié; J. Organometal. Chem. 30(1971) C70.

89. Yu.A. Aleksandrov, G.A. Razuvaev and G.N. Figurova; J. Organometal. Chem., 27 (1971) 207.

90. G.N. Figurava and Yu.A. Aleksandrov; Zh.Obshch.Khim., 40 (1970) 2334; Chem.Abstr., 74 (1971) 142003e.

91. H. Schumann and H.J. Breunig; J.Organometal. Chem., 27 (1971) C28.
92. J.W. Anderson and J.E. Drake; J.Chem.Soc.D, (1971) 1372.
93. K.S. Mazdiyasni, B.J. Schaper and L.M. Brown; Inorg.Chem., 10 (1971) 889.
94. J.D. Citron; J. Organometal. Chem., 30 (1971) 21.
95. M.M.G. Dousse and J. Satgé; Recl. Trav. Chim. Pays-Bas, 90 (1970) 221.
96. J.W. Anderson and J.E. Drake; Inorg.Nucl.Chem.Lett., 7 (1971) 1007.
97. M.E. Peach and H.G. Spinney; Can.J.Chem., 49 (1971) 644.
98. I.A. Vostokov, V.T. Bychkov and Yu.I. Dergunov; Zh.Obshch. Khim; 41 (1971) 1572; Chem. Abstr., 75 (1971) 129905b.
99. A.N. Egorochkin, E.N. Gladyshev, S.Ya.Khorshev, P.Ya.Bayushkin, A.I. Burov and N.S. Vyazankin; Izv. Akad. Nauk SSSR, Ser.Khim., (1971) 639; Chem. Abstr., 75 (1971) 36265c.
100. J.L. Wardell, R.D. Taylor and T.J. Lillie; J. Organometal. Chem. 33 (1971) 25.
101. N.S. Vyazankin, M.N. Bochkarev and A.I. Charov; J.Organometal. Chem., 27 (1971) 175.
102. M.A. Ignatenko, V.A. Ponomarenko and G.B. Frolova; USSR Pat. 301, 338; Chem.Abstr., 75 (1971) 63978u.
103. L.K. Garsia, M.A. Kazankova and L.F. Lutsenko; Zh.Obshch.Khim., 41 (1971) 1879; Chem.Abstr., 75 (1971) 151882p.
104. T.L. Tursunbaev, Z.M. Manulkin and A.N. Tatarenko; Zh.Obshch. Khim., 41 (1971) 865; Chem.Abstr., 75 (1971) 49251v.
105. J. Dubac, P. Mazerolles, A. Laporterie and P. Lix; Bull.Soc. Chim. Fr., (1971) 125.
106. N.S. Nametkin, S.G. Durgar'yan, L.I. Tikhonova and V.G.Filippova Vysokomol. Soedin., Ser.A, 13 (1971) 168; Chem.Abstr., 74 (1971) 76697f.
107. N.S. Nametkin, S.G. Dourgarian, L.I. Tikhonova and V.G.Filippova Bull.Soc.Chim.Fr. (1971) 656.
108. K.A. Makarov, T.K. Solov'eva and A.F. Nikolaev; Izv.Vyssh. Ucheb.Zaved.Khim. Khim.Tekhnol, 14 (1971) 763; Chem.Abstr. 75 (1971) 88984f.
109. W.R. Cullen and M.C. Waldman; J.Fluorine Chem., 1 (1971) 41; Chem.Abstr., 75 (1971) 110387n.

110. V.S. Zavgorodnii, E.S. Sivenkov and A.A. Petrov; Zh.Obshch. Khim., 41 (1971) 1577; Chem.Abstr., 75 (1971) 129900w.

111. A.I. Vil'davskaya, K.B. Rall and A.A. Petrov; Zh.Obshch. Khim., 41 (1971) 1279.

112. I.M. Gverdtsiteli, L.V. Baramidze and N.V. Tsikaridze; Zh.Obshch. Khim., 41 (1971) 139; Chem. Abstr., 75 (1971) 36266d.

113. I.A. Aslanov and S.Sh. Verdieva; Zh.Obshch.Khim., 40 (1970) 1266; Chem.Abstr., 74 (1971) 31817d.

114. I.A. Shikhiev and S.F. Karaev; Uch.Zap. Azerb.Gas.Univ., Ser.Khim.Nauk, (1969) 81; Chem. Abstr., 75 (1971) 6038p.

115. R.J.P. Corriu and J.J.E. Moreau; J.Chem.Soc.D, (1971) 812.

116. D. Seyferth and D.L. White; J. Organometal. Chem., 32 (1971) 317.

117. S.V. Ponomarev, M.B. Erman, S.A. Lebedev, S.Ya.Pechurina and I.F. Lutsenko., Zh.Obshch.Khim., 41 (1971) 127; Chem.Abstr., 75 (1971) 20541d.

118. T.A. Manukina, G.P. Kolyukhina, G.S. Burlachenko, I.F.Lutsenko and Yu.I. Baukov; Zh.Obshch.Khim., 40 (1970) 2607, Chem.Abstr., 75 (1971) 36272c.

119. D. Seyferth, H.Shih, P. Mazerollès, M. Lesbre and M.Joanny; J. Organometal.Chem., 29 (1971) 371.

120. M. Massol, D. Mesnard, J. Barrau and J. Satgé; C.R.Acad. Sci., Ser.C, 272 (1971) 2081.

121. J. Barrau, M. Massol, D. Mesnard and J. Satgé; J.Organometal, Chem., 30 (1971) C67.

122. P. Rivière and J. Satgé; Angew.Chem.Int.Ed., 10 (1971) 267.

123. N.S. Nametkin, L.E. Gusel'nikov, R.L. Ushakova, V.Yu.Orlov, O.V. Kuz'min and V.M. Vdovin; Dokl.Akad.Nauk SSSR, 194 (1970) 1096; Chem.Abstr., 74 (1971) 42440b.

124. C.H. Yoder and J.J. Zuckerman; Prep. Inorg. React., 6 (1971) 81; Chem. Abstr., 75 (1971) 118355w.

125. V.F. Mironov, S.A. Mikhailyants and T.K. Gar; USSR Pat. 268, 424; Chem. Abstr., 74 (1971) 88124e.

126. D. Seyferth; Pure Appl. Chem., 23 (1970) 391; Chem.Abstr., 74 (1971) 100137w.

127. D. Seyferth and S.B. Andrews; J. Organometal. Chem., 30 (1971) 151.

128. J. Lorberth; J. Organometal. Chem. 27 (1971) 303.

129. T.N. Brevnova, O.F. Rachkova and N.S. Vyazankin; Zh.Obshch. Khim., 40 (1970) 1760; Chem. Abstr., 74 (1971) 42448k.

130. J. Jappy and P.N. Preston., Inorg.Nucl. Chem.Lett., 7 (1971) 181.

131. Yu.I. Baukov, O.V. Dudnkina and I.F. Lutsenko; Zh.Obshch. Khim., 40 (1970) 2766; Chem. Abstr., 75 (1971) 20478p.

132. M. Krumpolc and V. Chvalovský; Syn.Inorg.Metal-Org.Chem., 1 (1971) 51; Chem.Abstr., 75 (1971) 36271b.

133. H. Oikawa and K. Kubo; Jap.Pat. 71 - 02, 498; Chem.Abstr., 75 (1971) 6108m.

134. Yu.I. Dergunov and I.A. Vostokov; Zh.Obshch.Khim., 41 (1971) 1647; Chem.Abstr., 75 (1971) 98640e.

135. I.A. Vostokov and Yu.I.Dergunov; Zh.Obshch.Khim. 40 (1970)1666.

136. P. Jutzi and F.W. Schroeder; Angew. Chem., Int.Ed.Engl., 10 (1971) 339.

137. M. Massol, J. Barrau, P.Rivière and J.Satgé; J. Organometal. Chem., 30 (1971) 27.

138. P. Rivière and J. Satgé; C.R.Acad.Sci., Ser.C, 272 (1971) 413.

139. T.N. Brevnova, O.F.Rachkova, N.S.Vyazankin, S.Kh.Ratushnaya and G.N. Bortnikov; Zh.Obshch.Khim, 41 (1971) 600; Chem. Abstr., 75 (1971) 49248z.

140. K. Moedritzer in E. Becker and M. Tsutsui (Eds), "Organometallic Reactions Vol.2", Wiley-Interscience, New York, p.1.

141. Ya.G. Zueva, N.V. Luk'yankina, V.A.Ponomarenko and A.V. Ignatenko; Izv.Akad.Nauk SSSR, Ser.Khim., (1971) 1128; Chem.Abstr. 75 (1971) 49249a.

142. Z. Pacl, M. Jakoubková, Z.Papouskova and V. Chvalovský; Collect.Czech.Commun., 36 (1971) 1568.

143. Z. Pacl, M. Jakoubková, V. Bažant and V. Chvalovský; Collect.Czech.Commun., 36 (1971) 1682.

144. Z. Pacl, M.Jakoubková, R. Řeřicha and V. Chvalovsky; Collect.Czech. 36 (1971) 2181.

145. V. Chvalovský, M. Jakoubkova and J. Syrček; Collect.Czech. Commun., 36 (1971) 2378.

146. W.L. Jolly; Inorg.Chem., 10 (1971) 2364.

147. A.N. Egorochkin, N.S. Vyazankin, S.Ya.Khorshev, S.E.Skobeleva, V.A. Yablokov and A.P. Tarabarina; Dokl.Akad.Nauk SSSR, 194 (1970) 1326.

148. I.Ya.Shtraus, L.A. Mai, G.Ya. Zueva and G.V. Borisyuk; Izv.Akad.Nauk, SSSR, Ser.Khim., 20(1971) 40;Chem.Abstr. 75 (1971) 11867n.

149. J.M. Bellama, S.O. Wandiga and A.A. Maryott; Inorg.Nucl.Chem. Lett., 7 (1971) 71.

150. M.G. Voronkov and L.A. Zhagata; Zh.Obshch. Khim, 41 (1971) 1776.

151. M.G. Voronkov and L. Zhagata; Zh.Obschch.Khim., 40 (1970) 1549; Chem.Abstr., 75 (1971) 4929f.

152. C. Eaborn, R. Eastmond and D.R.M. Walton, J.Chem.Sco.B, (1971) 127.

153. I.P. Beletskaya, K.P. Butin and O.A. Reutov; J.Organometal. Chem.Rev.A, 7 (1971) 51.

154. G.R. Dobson and E.P. Ross; Inorg.Chim.Acta, 5 (1971) 199.

155. Yu.A. Aleksandrov, B.I. Tarunin and V.A. Shushunov; Kinet. Katal., 12 (1971) 898; Chem.Abstr., 75 (1971) 151024k.

156. M. Gielen, J. Nasielski and G. Vandendunghen; Bull.Soc.Chim. Belges, 80 (1971) 165.

157. D.S. Boak, N.J. Friswell and B.G. Gowenlock; J.Organometal. Chem. 27 (1971) 333.

158. B.J. Aylett; Progr.Sterochem., 4 (1969) 213; Chem.Abstr., 4 (1969) 36329f.

159. F.R. Jensen and D.D. Davis; J.Amer.Chem.Soc., 93 (1971) 4047.

160. H. Sakurai and K. Mochida; J.Chem.Soc.D, (1971) 1581.

161. Quac Dang Chue; Vestn.Mosk.Univ.Khim., 12 (1971) 307; Chem.Abstr., 75 (1971) 81008g.

162. Yu.Kh.Shaulov, A.K. Fedorov, G.Ya.Zueva, G.V.Borisyuk and V.G. Genchel; Zh.Fix.Khim. 44 (1970) 2081; Chem.Abstr., 74 (1971) 7230m.

163. K.G. Kochetikhina, G.A. Domrachev and G.A. Razuvaev; Zh.Obshch. Khim., 40 (1970) 1273; Chem.Abstr., 74 (1971) 53945w.

164. K.G. Kochetikhina; Uch.Zap.Gor'k.Gas.Univ., (1970) 51; Chem. Abstr., 74 (1971) 124583q.

165. A.K. Goncharov, M.Kh.Karapet'yants and T.K. Gar; Zh.Fix. Khim. 45(1971) 184; Chem.Abstr., 74 (1971) 80064q.

166. A.G. Brook, P.J. Dillon and R. Pearce; Can.J.Chem., 49 (1971) 133.

167. R.J. Isabel and W.A. Guillory; J.Chem.Phys., 55 (1971) 1197.

168. Yu.A.Aleshonkova, L.N. Zhuravleva and A.D. Plotnikova; Zu.Prikl.Spektrosk., 13 (1970) 563; Chem.Abstr., 74 (1971) 17439a.
169. H.M. Seip; J.Chem.Phys., 54 (1971) 440.
170. R.D. Baechler and K. Mislow; J.Amer.Chem.Soc., 93 (1971) 773.
171. R.J. Cook and K. Mislow; J.Amer.Chem.Soc., 93 (1971) 6703.
172. D. Seyferth and D.L. White; J.Organometal Chem., 26 (1971) C15.
173. Yu.M. Tyurin, V.N. Flerov and V.K. Goncharuk; Zh.Obshch. Khim., 41 (1971) 494.
174. C.L. De Ligny and N.G. Van der Veen; Recl.Trav.Chim., Pays-Bas, 90 (1971) 984.
175. K. Ramaswamy and V. Balasubramanian; Indian J.Phys., 43(1969) 735; Chem.Abstr., 75 (1971) 75944t.
176. A.A. Perov and S.E. Kupriyanov; Khim. Vys.Energ., 4 (1970) 551; Chem.Abstr., 74 (1971) 26633m.
177. M.G. Voronkov, M.V. Pozdnyakova and L.A. Zhagata; Zh.Obshch. Khim., 40 (1970) 1425.
178. A. Breeze, G.A.D. Collins and D.W.J. Cruickshank; J.Chem.Soc.D, (1971) 445.
179. J.M. Jerkunica and T.G. Taylor; J.Amer.Chem.Soc., 93 (1971) 6278.
180. Chan - Cheng Su; J.Amer.Chem.Soc., 93 (1971) 5653.
181. R.M. Dreyfuss and W.L. Jolly; Inorg.Chem., 10 (1971) 2567.
182. D. Quane; J. Inorg.Nucl.Chem., 33 (1971) 2722.
183. J.R. Durig and C.W. Hawley; J.Phys.Chem., 75 (1971) 3993.
184. B. Fontal and T.G. Spiro; Inorg.Chem., 10 (1971) 9.
185. R.J.H. Clark and C.J. Willis; Inorg.Chem. 10 (1971) 1118.
186. R.J.H. Clark and B.K. Hunter; J.Chem.Soc.A, (1971) 2999.
187. W. Kiefer and H.W. Schroetter; Z. Naturforsch.B, 25 (1970) 1374.
188. T. Birchall and I. Drummond; J.Chem.Soc.A, (1971) 3162,
189. G.K. Barker, J.E. Drake, R.T. Hemmings and B. Rapp; J.Chem. Soc.A, (1971) 3291.
190. J.W. Anderson, G.K. Barker, J.E. Drake and R.T. Hemmings; Can.J. Chem., 49 (1971) 2931.
191. J.R. Durig, C.F. Jumper and J.N. Willis; J.Mol.Spectrosc., 37 (1971) 260. Chem.Abstr., 74 (1971) 69944f.
192. A. Marchand, T.M. Forel, M.Lebedeff and J. Valade; J.Organometal.Chem., 26 (1971) 69.

193. J.R. Durig and J.B. Turner; Spectrochim.Acta, A, 27 (1971) 1623.

194. J.R. Durig and J.B. Turner, Spectrochim.Acta, A, 27 (1971) 395.

195. S.R. Stobart; Inorg.Nucl.Chem.Lett., 7 (1971) 219.

196. D.J. Cardin, S.A. Keppie, M.F. Lappert, M.R. Litzow and T.R. Spalding; J.Chem.Soc.A, (1971) 2262.

197. A.I. Kakhniashvili and D.Sh.Ioramashvili; Zh.Obshch.Khim., 40 (1970) 1552 Chem.Abstr., 75 (1971) 6039q.

198. A.I. Kakhniashvili and D.Sh.Ioramashvili; Zh. Obshch.Khim., 40 (1970) 1556; Chem.Abstr., 75 (1971) 6036m.

199. O.I. Kaptyug and M.D. Stadnichuk; Zh.Obshch.Khim., 40 (1970) 1293; Chem.Abstr. 74 (1971) 53944v.

200. T.F. Schaaf and J.P. Oliver; J. Organometal. Chem., 32 (1971) 307.

201. J.E. Drake, R.T. Hemmings and C. Riddle; J.Chem.Soc.A, (1971) 600.

202. K. Moedritzer; Z. Naturforsch. B, 26 (1971) 517.

203. Yu.I. Baukov, G.S. Burlachenko, A.S. Kostyuk and I.F.Lutsenko; Zh.Obshch.Khim., 40 (1970) 707.

204. F.C. Shaw and A.L. Allred; J.Organometal.Chem., 28 (1971) 53.

205. K.M. Mackay and S.R. Stobart; Spectrochim.Acta, A, 27 (1971) 923.

206. D. Rosenberg and W. Drenth; Tetrahedron, 27 (1971) 3893.

207. P.G. Harrison, S.E. Ulrich and J.J. Zuckerman; J.Amer.Chem. Soc., 93 (1971) 2307.

208. R.E. Hess, C.K. Hass, B.A. Kaduk, C.D. Schaeffer and C.H.Yoder; Inorg.Chim.Acta, 5 (1971) 161; Chem.Abstr., 75 (1971) 103372a.

209. S.R. Stobart; J. Organometal.Chem., 33 (1971) C11.

210. Yu.A.Ustynyuk and A.V. Kisin; J.Organometal.Chem., 33 (1971) C61.

211. H. Schmidbaur and G. Kammel; Chem.Ber., 104 (1971) 3252.

212. P. Jutzi; Chem.Ber., 104 (1971) 1455.

213. A.N. Nesmeyanov, N.E. Kolobova, V.V. Skripkin, K.N.Anisimov and L.A. Fedorov; Dokl.Akad.Nauk SSSR, 195 (1970) 368; Chem.Abstr., 74 (1971) 42439h.

214. H.L. Tigelaar and W.H. Flygare, Chem.Phys.Lett., 7 (1970) 254; Chem.Abstr., 74 (1971) 59143e.

215. E.G. Ermakova, T .L. Krasnova, A.M. Mosin, M.I. Onoprienko, E.A. Chernyshev and M.T. Shpak; Ukr.Fix.Zh., 16 (1971) 900; Chem.Abstr., 75 (1971) 135294t.

216. W.K. Musker and R.L. Scholl; J. Organometal.Chem., 27 (1971) 37.

217. J.G. Kenworthy, J. Myatt and M.C.R. Symons; J.Chem.Soc.A, (1971) 3428.

218. P.J. Krusic and J.K. Kochi; J.Amer.Chem.Soc., 93 (1971) 846.

219. M. Fishwick and M.G.H. Wallbridge; J.Chem.Soc.A, (1971) 57.

220. M.F. Lappert, J.B. Pedley, J. Simpson and T.R. Spalding; J. Organometal Chem., 29 (1971) 195.

221. M.Gielen, J. Nasielski and G. Vandendunghen; Bull.Soc.Chim. Belges, 80 (1971) 175.

222. D.J. Harvey, M.G. Horning and P. Vouros; Org.Mass Spectrom., 5 (1971) 599; Chem.Abstr., 75 (1971) 42029v.

223. R.E. Sacher; Diss.Abstr.Int.B, 31 (1970) 3310; Chem.Abstr., 75 (1971) 75589f.

224. P.J. Bassett and D.R. Lloyd; J.Chem.Soc.A, (1971) 641.

225. S. Cradock and E.A.V. Ebsworth; J.Chem.Soc.D, (1971) 57.

226. S. Cradock; Che.Phys.Lett. 10 (1971) 291; Chem.Abstr. 75 (1971) 124831q.

227. J.C. Green, M.L.H. Green, P J.Joachim, A.F. Orchard and D.W. Turner; Phil.Trans.Roy.Soc. London, A, (1970) 111; Chem.Abstr. 74 (1971) 58936d.

228. E. Maslowsky; Chem.Rev., 71 (1971) 507.

229. K.L. Watters, W.M. Butler and W.M. Risen; Inorg.Chem., 10 (1971) 1970.

230. P.P. Gaspar, K.Y. Choo, E.Y.Y. Lam and A.P. Wolf; J.Chem.Soc.D, (1971) 1012.

231. D. Potts and A. Walker; Can.J.Chem., 49 (1971) 2171.

232. D. Potts and A. Walker; Can.J.Chem., 49 (1971) 202.

233. N.I. Gapotschenko, Yu.T.Struchkov, N.V. Alekseev and I.A. Ropova; Zh.Strukt.Khim., 12 (1971) 571; Chem.Abstr. 75 (1971) 134110t.

234. A. Kemme, J. Bleidelis, R.P. Shibaeva and L.O. Atovmyan; Khim.Geterotsikl.Soedin, (1970) 1145; Chem.Abstr., 74 (1971) 58158b.

235. J. Howard and P. Woodward; J.Chem.Soc.A, (1971) 3648.

236. M.Ziegler and J.Weiss; Z.Naturforsch.,B, 26 (1971) 735.

237. P.C. Chieh; J.Chem.Soc.A, (1971) 3243.

238. R.J.D. Gee and H.M. Powell; J.Chem.Soc.A, (1971) 1956.

239. S.I. Obtemperanskaya and I.V. Dudova; Vestn.Mosk.Univ.Khim., 11 (1970) 461; Chem.Abstr., 74 (1971) 9408z.

240. G.N. Bortnikov, A.V. Kiselev, N.S. Vyazankin and Ya.I.Yashin; Chromatographia, 4 (1971) 14; Chem.Abstr. 74 (1971) 112148p.

241. G.N. Bortnikov, N.S. Vyazankin, E.N. Gladyshev and Ya.I.Yashin; Izv.Akad.Nauk SSSR, Ser.Khim., (1970) 1661; Chem.Abstr., 74 (1971) 27652u.

242. G.M. Bortnikov, M.N. Bochkarev, N.S. Vyazankin, S.Kh. Ratushnaya and Yu.I.Yashin; Izv.Akad.Nauk SSSR Ser.Khim., (1971) 851; Chem.Abstr. 75 (1971) 49240r.

243. A.G. Davies; Brit.Pat. 1,234,779; Chem.Abstr., 75 (1971) 64900z.

244. V.N. Myakov, B.B. Troitskii and G.A. Razuvaev; Sintez. Issled. Eff. Khimikatov Polim. Mater., (1969) 184; Chem.Abstr., 75 (1971) 77460f.

245. L. Roos; Ger.Offen.1, 915,571; Chem.Abstr. 74 (1971) 26664x.

246. L.E. Contois; Ger.Offen. 1, 942,421; Chem.Abstr., 74 (1971) 8351p.

247. M.J. Hammond J.W. Haynes, R.F. Herner, J.E. Mathers, E. J. Mehalchick and F.F. Mikus; Ger.Offen. 2,009, 101; Chem.Abstr., 74 (1971) 36209s.

248. W.R. Young, I. Heller and D.C. Green; Mol.Cryst.Liquid Cryst., 13 (1971) 305; Chem.Abstr., 75 (1971) 123297h.

249. K.Asahi and K. Makabe; Jap.Pat. 71-02,964; Chem.Abstr., 74 (1971) 125852p.

250. S. Sakai, K. Itoh and Y. Ishii; Yuki Gosei Kagaku Kyokai Shi, 28 (1970) 1109; Chem.Abstr., 74 (1971) 141918v.

251. N.S. Stroganov, V.G. Khobot'ev and L.V. Kolosova; Vop.Vod. Toksikol., (1970) 66; Chem.Abstr., 74 (1971) 121801y.

252. A.K. Sijpesteijn; J.Microbiol.Serol. 36 (1970) 335; Chem.Abstr. 74 (1971) 39655v.