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STRUCTURAL ORGANOGERMANIUM CHEMISTRY

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I. Introduction

Within the chemistry of the organometallic compounds of the main-group elements, perhaps no area has received more attention than that of the lower cogeners to carbon in Group IV. In particular, the ability of silicon to form catenated species and to mimic the organic chemistry of carbon on the one hand and the extensive structural chemistry of the organotins on the other has given rise to volumes of research publications. Notable, however, by its relative paucity, is the extent of interest in the organometallic chemistry of germanium. This is nowhere more apparent than in the structural chemistry of these species, which is perhaps made more surprising in view of the structural crossroads occupied by this class of compounds, separating the predominantly carbonoid chemistry of silicon from the metallic elements tin and lead.

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Despite this, the available data present a number of interesting features which merit review, a review which we feel is timely both from the recent absence of any similar collective article [although annual reviews do provide a yearly assessment of current interest in the field (*11*)] and in view of the current explosion of structural studies resulting from the relative ease with which diffraction data can now be collected and manipulated.

In presenting this current review of structural organogermanium chemistry our aim is threefold. First, to provide a collective database summarizing Ge–element bond lengths and molecular geometries which can be used subsequently for comparative purposes. Second, the higher volatility of many organogermanium compounds compared to those of the lower members of Group IVA has led to a relatively balanced application of diffraction techniques to the structural problem, thus affording a number of opportunities to compare both solid (X-ray diffraction) and gaseous state (electron diffraction and microwave spectroscopy) structures for the same compound. Finally, to compare and contrast the data with that available for analogous organosilicon (*128*) and organotin (*49, 185*) compounds, so that structural trends within the group might be established.

The article is sectionalized by periodic group to which the atom directly bonded to the R_nGe moiety belongs, the transition elements being treated collectively. Derivatives of divalent germanium are reviewed separately. With the exception of the organogermanium hydrides, no entries are recorded for derivatives of main Groups I, II, and III, highlighting this as an area for further study. The literature has been covered up to the end of 1981 with an addendum updating the article, and includes those compounds reviewed by Bokii and Struchkov in 1968 (*22*).

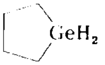
II. Organogermanium Hydrides

Several volatile organogermanium hydrides have been studied, principally to compare their barrier to internal rotation about the Ge—C bond with the analogous C—C and Si—C compounds. Although analysis of the microwave spectroscopic data which predominate in these studies often requires one or more of the molecular parameters to be assumed, the data taken as a whole indicate a number of trends in the bonding of these simple tetrahedral molecules (Table I).

Comparison of the structures of mono- (*120*), di- (*161*), and trimethylgermane (*62*) indicates no systematic variation in the Ge—C bond

TABLE I

BOND DISTANCES (Å) AND ANGLES (DEGREE) IN ORGANOGERMANIUM HYDRIDES[a]

Compound	Ge—H	Ge—C	H—Ge—H	C—Ge—C	H—Ge—C	Reference
CH_3GeH_3	1.529	1.9453	109.3			*120*
$(CH_3)_2GeH_2$		1.950		110.0		*161*
$(CH_3)_3GeH$	1.532	1.947		109.6	109.3	*62*
CH_3GeH_2F		1.935				*114*
		1.925				*145*
$ClCH_2GeH_3$	1.517				107.75	*133*
$C_2H_5GeH_3$	1.522	1.949			109.7	*67*
$CH_2{=}CHGeH_3$	1.520	1.926			109.7	*65*
$HC{\equiv}CGeH_3$	1.521	1.896	109.9			*160*
				98		*162*
$(C_5H_5)GeH_3$		1.969[b]				*14*
		1.965[c]				*14*
$(o\text{-}CH_3C_6H_4)_3GeH$	1.700	1.980[d]		99–110	102–116	*36*
GeH_4	1.528		109.5			*126*
$R_2(C_2H_5O)GeH$[e]	1.46	1.953		114.5	108	*118*
		1.969			120	

[a] All data pertain to the gaseous state, derived from microwave spectroscopic data, unless indicated otherwise.

[b] Gas phase, electron-diffraction data.

[c] Solid-state, X-ray crystallographic data.

[d] Mean value.

[e] $R = [(CH_3)_3Si]_2CH—$.

length (mean value 1.948 Å), behavior paralleled in the corresponding silanes [Si—C = 1.867 Å (*106, 107, 141*)] and hydrocarbons (*123, 124*). The Ge—H bond length (mean value 1.531 Å) and C—Ge—C angle (mean value 109.8°) also show no systematic variation within the series, although the relevant silanes (*106, 107, 141*) and hydrocarbons (*123, 124*) show a slight increase in the bond length and a decrease in the bond angle with increased organic-group substitution.

Substitution of a hydrogen directly bonded to germanium in methylgermane by fluorine results in a decrease in Ge—C bond length (Table I), although the extent of this decrease, which presumably arises from isovalent rehybridization (*16*) in which the *p*-dominated Ge—F bond allows an increase in the *s*-character of the Ge—C bond, varies among authors (*114, 145*) depending on the method of data manipulation. It is interesting to note that the decreased Ge—C bond length in

CH_3GeH_2F relative to CH_3GeH_3 does not increase the barrier to rotation about this bond, although within the series CH_3EH_2F (E = C,Si,Ge), the potential energy barrier to rotation about the C—E bond does decrease with increasing E—C bond length, as expected (*145*).

When halogen substitution occurs *within* the organic group of the organogermane, the increased electronegativity of the organic moiety results in an increase in the Ge—C bond length, for example, from 1.945 Å in CH_3GeH_3 (*120*) to 1.961 Å in $ClCH_2GeH_3$ (*133*), and a decrease in the Ge—H bond length from 1.529 to 1.517 Å for the same pair of compounds, both trends following the pattern expected from simple rehybridization arguments (*16*). Methyl- (*106*) and chloromethylsilane behave analogously (*75, 153*).

The Ge—C bond length is also a function of the hybridization at carbon, as seen in the structures of ethylgermane (*67*), vinylgermane (*65*), and germylacetylene (*160*). A gradual decrease occurs, from 1.949 Å in ethylgermane (*67*) to 1.926 Å in vinylgermane (*65*) and 1.896 Å in germylacetylene (*160*), paralleling an increase in *s*-content in the Ge—C bond as the hybridization at carbon changes from sp^3 to sp^2 and finally to *sp*. This compares with a contraction of 0.7 Å in the C—C bond between methylacetylene (*165*) and *n*-propane (*123*) and with a shortening of the Si—C bonds of 0.015 Å going from methylsilane (*106*) to vinylsilane (*135*). The Ge—H bond in all three of the above organogermanes is identical (Table I), and is apparently unaffected by the hybridization of carbon in the adjacent Ge—C bond.

Despite the experimental difficulties inherent in the crystallation of highly volatile compounds, the structure of germylcyclopentadiene has been studied by both electron diffraction in the gas phase and by X-ray diffraction at low temperature (160 K) in the solid state (*14*). It is possible for the germanium to be η^1 bonded to a monohapto ring, as silicon is in silylcyclopentadiene (*17*), or η^5 bonded to a pentahapto ring as evidenced by beryllium in cyclopendtadienyl(methyl)beryllium (*61*), the former structure being indicated by NMR data (*9*) and now confirmed in both phases by diffraction data. The shortest Ge—C contact in both structures is the same (1.967 Å), although it should be borne in mind that the two techniques measure different molecular entities, electron diffraction measuring the average internuclear separation while X-ray diffraction distances are the separation of the mean positions of the centers of electron density. Contacts to the next nearest carbons in the ring (~2.80 Å) are too long to be considered bonding, and the pattern of long, short, medium, short, long C—C distances around the ring from C-1 (Fig. 1) reflects a localization of the two π-bonds between the C-2 and C-3 and the C-4 and C-5 ring positions. The

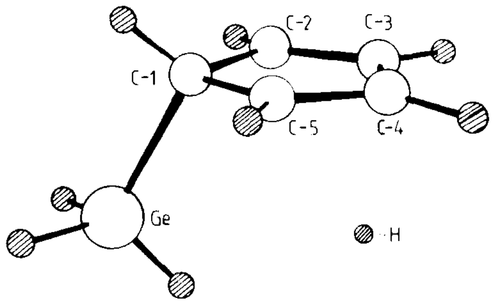


FIG. 1. General view of the $H_3Ge(\eta^1\text{-}C_5H_5)$ showing the labeling scheme.

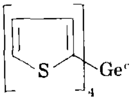
homocyclic ring is essentially planar, the dihedral angle between the planes C-2—C-1—C-5 and C-2—C-3—C-5 (Fig. 1) being 4° in the crystal and 1° in the gas. Silylcyclopentadiene also contains a planar ring (*17*), while electron diffraction data for trimethylsilyl- (*172*) and trimethylgermylcyclopentadiene (*173*) indicate significant deviations from planarity for the aromatic moiety. The lack of donor–acceptor sites within the molecule precludes close approach of molecules in the solid state, and packing interactions leave the molecular structure essentially unperturbed.

Bond angles within the gaseous organogermanes are internally consistent for each of the three angle types, namely, H—Ge—H, C—Ge—C, and H—Ge—C (Table I). Two exceptions however merit comment. First, the H—Ge—C angle in $ClCH_2GeH_3$ is reduced by almost 2° from ~109.5 to 107.75° (*133*), an observation which corroborates the proposed rehybridization of bonds about germanium to simultaneously increase the *p*-content of the Ge—C bond and the *s*-content of the Ge—H bond (*vide supra*). Second, the C—Ge—C bond angle within germacyclopentane is reduced to 98° as a consequence of unequal bond lengths within the ring (*162*), although direct comparison of this species with linear organogermanes is inappropriate.

The crystal structure of tri-*o*-tolylgermanium hydride (*36*) is that of a badly distorted tetrahedron, although detailed interpretation of the bond lengths and angles is clouded by the quality of the data, which, because of crystal twinning, could only be refined to an *R* value of 14%. The molecule is sterically hindered, with the methyl group from each organic residue crowding close to the germane hydrogen atom. Consequences of the crowding about the central atom are a range of C—Ge—C angles (98.7–110.3°), distortions in the bond angles at the *o*-carbon atoms which bear the methyl groups, and long Ge—C (mean value 1.980 Å) and Ge—H (1.700 Å) bonds.

TABLE II

GERMANIUM–CARBON BOND LENGTHS (Å) IN SYMMETRICAL TETRAORGANOGERMANES

Compound	Ge—C	C—Ge—C	Reference
$(CH_3)_4Ge^a$	1.945	*b*	*91*
$(CF_3)_4Ge^a$	1.989	*b*	*136*
$(C_6H_5)_4Ge^c$	1.9537^d	108.8(2), 109.8	*42*
	1.954	108.8(2), 109.8	*41*
	1.957	109.0	*102*
$(C_6F_5)_4Ge^c$	1.957	105.0(2), 111.7	*101*
	1.94	111.5	*103*

[a] Electron diffraction.
[b] Tetrahedral geometry assumed.
[c] X-Ray crystallography.
[d] Mean of two values [1.9559(5) and 1.9515(6) Å] obtained from differing modes of data collection.

The shortest Ge—H bond yet found in an organogermane occurs in the recently reported complex hydride $\{[(CH_3)_3Si]_2CH\}_2(OC_2H_5)GeH$ (*118*). The shortness of the Ge—H bond (1.46 Å) must, at least in part, arise from the hybridization demands of the electronegative ethoxy group. Distortions in the tetrahedral environment about the germanium (Table I) arise from the steric requirements of the bis(trimethylsilylmethyl) moieties, while the authors attribute to the same source the stability of this compound with respect to the reductive elimination of alcohol normally observed (*127*).

III. Group IVA Derivatives

A. SYMMETRICAL TETRAORGANOGERMANES

The structures of the simple, tetrahedral, symmetrical tetraorganogermanes serve both as the best measures of Ge—C bond lengths (Table II) unperturbed by the influence of atoms of varying electronegativity bonded to germanium, and also to assess the available theoretical models for the prediction of molecular packing in the solid state. It is somewhat surprising therefore that relatively few compounds of this type have been studied (Table II) compared with extensive interest in this aspect of the chemistry of tin (*49, 185*).

Brockway and Jenkins applied electron diffraction techniques as early as 1936 to determine a T_d geometry for $(CH_3)_4Ge$, and a Ge—C bond length of 1.98 Å (*31*). In the light of more recent microwave data which indicate a substantially shorter Ge—C bond length in the series of methylgermanes (*62, 120, 161*), this structure has been redetermined (*91*) to yield a more reliable Ge—C bond length of 1.945 Å.

When the more electronegative trifluoromethyl groups are bonded to germanium the Ge—C bonds lengthen to 1.980 Å (*136*). This is in good agreement with systematic force constant calculations which predict a Ge—C bond length of 1.98–2.00 Å for $(CF_3)_4Ge$ (*72*), but somewhat shorter than the value of 2.02–2.04 Å predicted on the basis of the electronegativity of the central atom (*182*). The four CF_3 groups stagger the corresponding Ge—C bond to preserve T_d symmetry, in accord with the calculations of the torsional potential (*90*) which predict an energy minimum at the staggered conformation and a maximum at ~10 kJ mol^{-1} higher in energy for the eclipsed arrangement (*136*).

The crystal structures of tetraphenylgermane (*41, 42, 102*) and its related pentafluorophenyl analog (*100, 101*) have been the subject of a number of reports. Both compounds exhibit $\bar{4}$ symmetry, and general agreement on bond angles and distances exists (Table II). The available data permit a comparison of a number of theoretical approaches to predicting molecular packing. Most successful among these is an approach (*102*) in which all intermolecular H ··· H contacts are computed for varying values of α, an angular measure of the degree of rotation of the phenyl ring about the Ge—C bond. Assuming that at the most favorable packing arrangement at least one H ··· H distance must be in the range 2.37–2.40 Å (*27*), with none less than 2.37 Å, the analysis yields a value of $\alpha = 54°$ for $(C_6H_5)_4Ge$, in good agreement with the experimental value of 54.1°, although a second conformation with $\alpha = 45°$ was also predicted, suggesting limitations to this simple analytical method.

Lattice constants and space groups have been reported for two crystal modifications of $(C_6H_5C{\equiv}C)_4Ge$ (*129*).

B. UNSYMMETRICAL TETRAORGANOGERMANES

1. *Simple Compounds*

Electron diffraction data for $(CH_3)_3GeC{\equiv}CCl$ and the analogous trimethylsilyl and *t*-butyl compounds show no differences in the length of

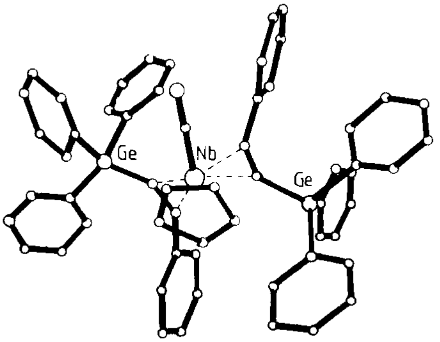


FIG. 2. The molecular structure of $[\eta^2\text{-}(C_6H_5)_3GeC{\equiv}CC_6H_5]_2Nb(CO)(\eta^5\text{-}C_5H_5)$.

the carbon–carbon multiple bond, thus ruling out resonance forms involving $d\pi$–$p\pi$ bonding in the organometallic compounds (*183*). No explanation is available for the long Ge—C≡C bond (1.930 Å) in the organogermylacetylene.

π Bond formation between the acetylene groups and niobium in $(\eta^5\text{-}C_5H_5)Nb(CO)(\eta^2\text{-}Ph_3GeC{\equiv}CPh)_2$ (Fig. 2) produces a lengthening of both the —C≡C— and Ge—C≡ bonds relative to $H_3GeC{\equiv}CH$ (Table I) and distortions of the linear Ge—C≡C—C moiety toward a *cis*-olefin geometry, both observations consistent with a rehybridization from *sp* to sp^2 at carbon (*110*).

Cyclopentadiene groups are invariably σ bonded to Ge(IV), although the geometry of the ring is less consistent. Thus, gaseous trimethylgermyl cyclopentadiene (*173*) shows a marked deviation from planarity for the aromatic ring with a envelope dihedral angle of 24°. In contrast, germylcyclopentadiene incorporates a planar ring in both gaseous and solid phases (see Section II). The symmetry demands on an $\eta^5\text{-}C_5H_5$ ring involved in a metal–ligand π interaction obviate the question of major distortions from ring planarity, and such an arrangement is maintained in the ferrocenophane, (1,1′-ferrocenediyl)diphenylger-

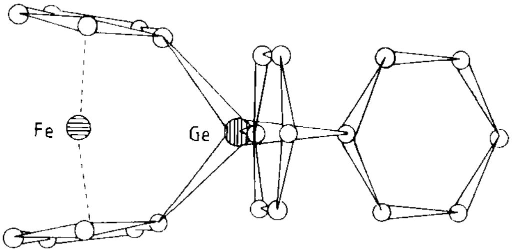
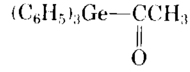


FIG. 3. The molecular structure of (1,1′-ferrocenediyl)diphenylgermane.

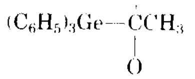
mane (Fig. 3). The single atom bridge between the two cyclopentadiene rings is, however, strained, and distortions in the geometry of the molecule as a whole manifest themselves in a tilting of the C_5H_4 rings relative to one another and in a closing of the bridging C—Ge—C angle by ~15° from the tetrahedral value of 109.5° (*156*).

The existence of two distinct types of Ge—C bond in acetyltriphenylgermane [Ge—C(phenyl) = 1.945; Ge—C(acetyl) = 2.011 Å] has been interpreted in terms of resonance structures involving ionic species, viz.



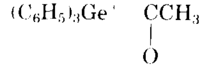
$(C_6H_5)_3Ge\text{—}\underset{\overset{\|}{O}}{C}CH_3$

(1A)



$(C_6H_5)_3Ge\text{—}\underset{\overset{|}{O}}{\overset{+}{C}}CH_3$

(1B)



$(C_6H_5)_3Ge^{+}\quad\underset{\overset{|}{O}}{C}CH_3$

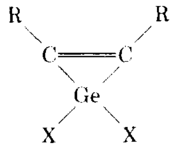
(1C)

While a significant contribution from **1C** to the overall structure is claimed (*89*), the difference in the two Ge—C bonds amounts to only 4σ, and suggests that such an interpretation is, at best, tentative.

In the related ketene, $[(CH_3)_3Ge]_2C{=}C{=}O$, electron diffraction data indicate a Ge—C(=C)—Ge angle of 127.6° (*149*), compared to 119.2° for the Ge—C(=O)—C angle in **1** (*89*), presumably arising from the increased steric bulk about the central sp^2 carbon, while phenyl(triphenylgermyl)diazomethane is isostructural with its silicon analog (*86*).

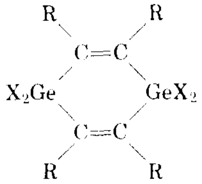
2. *Cyclic Derivatives*

The reaction between Ge(II) halides and carbon–carbon triple bonds yields oxidative addition products which can be either monomers (**2**) or dimers (**3**):



(**2**)

X = halogen



(**3**)

Alkylation or arylation of these species has been achieved via Grignard reactions, and the structural problem for representative members of both the tetraorgano- (*20, 21, 26, 176, 178*) and dihalodiorganogermane (see Section VI) series has been resolved.

A 1,4-digerma-1,1,4,4-tetraorganocyclohexa-2,5-diene structure (**3**) is adopted for both X = CH_3 (*26*) and C_6H_5 (*20, 21, 178*) in the solid. In

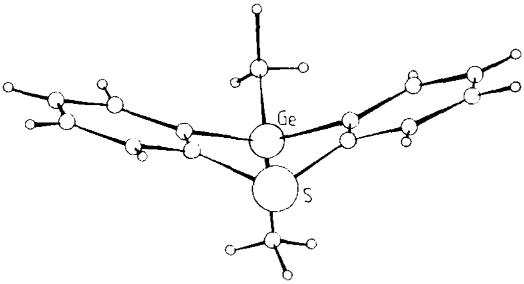


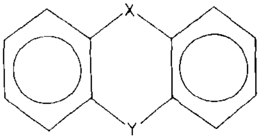
FIG. 4. Projection of the molecule 10,10-dimethyl-10-germa-9-thio-9,10-dihydroanthracene.

both compounds the heterocyclic ring is planar within experimental error (*26, 178*) in contrast to the analogous $[(CH_3)_2SiC_2(C_6H_5)_2]_2$, in which a slight tendency toward a chair conformation is observed (*178*). Ring planarity is, however, achieved only at the expense of endocyclic valence angle distortions at both carbon and germanium, while the observed equivalence of the endo- and exocyclic Ge—C bond lengths precludes $d\pi$–$p\pi$ interactions between germanium and the ring carbons (*21, 26*).

On the other hand, electron diffraction data for gaseous $(CH_3)_2GeC_2H_2$ (*176*) indicates a three-membered ring structure (**2**), despite the fact that mass spectral evidence indicates structure (**3**) in the vapor (*174*). Electron diffraction data for the corresponding dihalogermyl compounds (*176*) only cloud the issue, with the dichloro compound adopting structure (**3**) as it does in the solid (*179*), while the diiodide analog, which also has a dimeric structure in the crystal (*178*), is capable of existing in either of the structural forms (**2,3**) in the vapor (*176;* see Section VI).

The lattice parameters and space group have also been determined for $[(C_6H_5C)_2Ge(CH_3)_2]_n$ (n = 1,2?) (*25*), although the reliability of these data is questionable in the light of redeterminations of other data reported therein (*20, 26*).

The question of ($p \rightarrow d$)-π bonding and ring planarity also arises in compounds having an anthracene-like carbon skeleton substituted at either or both of the 9 and 10 positions by atoms bearing vacant d-orbitals (**4**). Heteroatom substitution in 9,10-bis(dimethylgermyl)-



(4)

TABLE III

ORGANOGERMYL ANTHRACENYL DERIVATIVES AND RELATED COMPOUNDS

X^a	Y^a	Butterfly angle (deg)^b	Mean Ge—C (Å)		Reference
			endo	exo	
$(CH_3)_2Ge$	$(CH_3)_2Ge$	151.6	1.96	1.95	*69*
—	$(CH_3)_2Ge$	180	1.98	1.91	*68*
S	$(CH_3)_2Ge$	143.6	1.934	1.927	*6*
CH_2CH_2	$(C_6H_5)Ge$	156	1.95	1.96	*45*
O	Cl_2Ge	170.5	1.90	—	*170*

^{a} Defined in (*4*).

^{b} The angle between the planes of the two C_6H_4 rings.

(*69*), 9-thio-10-dimethylgermyl- (*6*) (Fig. 4), and 9-methylene-10-diphenylgermyl-9,10-dihydroanthracene[1] (*45*) produces nonplanar structures, with "butterfly angles" in the range 143.6–156° (Table III). This evidence, when coupled with the near equality of the endo- and exocyclic Ge—C bond lengths, rules out any possibility of significant $d\pi$–$p\pi$ bonding.

Data for the related compounds 9,9-diphenyl-9-germafluorene and 9-oxa-10-dichlorogermyl-9,10-dihydroanthracene, are, however, less easily interpreted. Ring planarity is forced upon the fluorene derivative by the absence of a bridging atom at the 9 position of the anthracene skeleton, thereby affording the most favorable molecular architecture for heteroatom π bond participation. Contrary to expectation, however, the exocyclic Ge—C bonds are *shorter* than the endocyclic analogs (Table III), casting doubt upon the reliability of the data (*68*).

If *d*-orbital participation in bonding occurs to any significant extent in this series of compounds it does so in the 9-oxa-10-dichlorogermyl derivative, which, together with only a 9.5° deviation from ring planarity, exhibits the expected short (1.90 Å) endocyclic Ge—C bonds (*170*). Nonetheless, such a claim is made with justifiable caution in view of the absence of the same phenomena in both the fluorene (*68*) and 1,4-digermacyclohexa-2,5-dienes (*21*, *26*), whose ring planarity would seem even more favorably disposed to π bond formation.

Moreover, 2,3,4,5-tetraphenyl-1,1-diethynyl-1-germacyclopentadiene is also nonaromatic as evidenced by the alternating short (~1.35 Å) and long (~1.51 Å) C—C bond lengths within the five-membered ring, even though the germanium lies only ~0.1 Å out of the C_4 plane

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[1] Alternatively named 5,5-diphenyl-10,11-dihydro-5*H*-dibenzo[*b*,*f*]germepin.

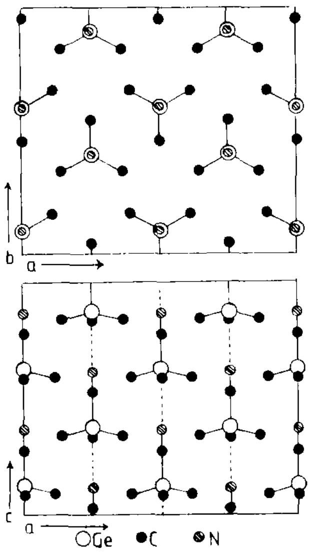


FIG. 5. The lattice structure of $(CH_3)_3GeCN$. Top view: along the *a* axis; bottom view: along the *b* axis.

(*125*). An additional feature of this molecule is the very short exocyclic Ge—C≡ bond (mean value 1.883 Å).

The structures of 6,6-dimethyl-6-germacycloundecanone (*73*), 1-methyl-1-germaadamantane (gas phase) (*154*), and two polycyclic germacarbosiloxanes (*76*) have been determined and incorporate the usual bond angles and distances. Cell parameters for 1,1-dimethyl-1-germa-6,7-cycloundacanediol have been reported (*29*).

3. *Tetraorganogermanes with Bridging Ligands*

Intra- and intermolecular interactions between lone-pair bearing atoms and potential Lewis acids play a paramount role in structure formulation, imparting both variety and variability to the coordination number and geometry at the donor–acceptor sites and ultimately influencing the chemical and physical properties of the species. Unfortunately, such interactions in the solid often occur at about the limits of van der Waals forces, inflicting ambiguity on even X-ray diffraction studies and leaving structural interpretation very much in the eye of the beholder. It might even be anticipated that such borderline situations would be common in the chemistry of germanium, in view of its location in the fourth group between the carbonoid chemistry of silicon and the metallic elements tin and lead.

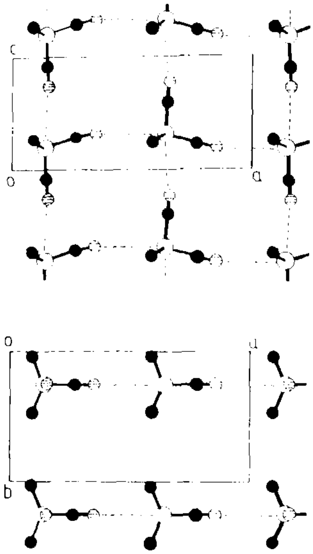


FIG. 6. Views of $(CH_3)_2Ge(CN)_2$, perpendicular (top view) and parallel (bottom view) to the plane of interacting molecules.

Problems of this nature, however, can be somewhat alleviated by the availability of complementary gas phase electron diffraction or microwave data, from which values for the crucial structural parameters uninfluenced by solid-state bonding and packing effects can be evaluated. Changes in these reference values coupled with a suggestive stereochemistry between the donor–acceptor components of the coordinate bond are often sufficient to confirm bonding. The utility of combined microwave spectroscopic and X-ray diffraction methods is amply illustrated by the cyano derivatives of di- and trimethylgermane.

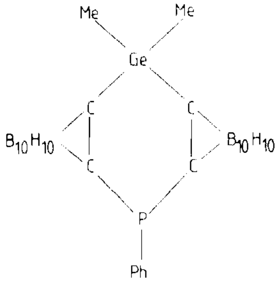
In crystals of trimethylcyanogermane, molecules align parallel to the *c* axis (Fig. 5), with the nitrogen atom of the cyanide group in one molecule pointing directly toward the germanium atom of the next, at a distance of 3.57 Å (*152*). A similar, but more extensive, stereochemical arrangement of Lewis acid and base components occurs in dimethyldicyanogermane (Fig. 6) with intermolecular contacts occurring at 3.28 and 3.84 Å (*112*). These distances are very close to what is assumed to be the van der Waals distance for such an interaction (~3.5 Å), although a reliable value for the van der Waals radius of germanium is apparently lacking. For such borderline interactions to be meaningful, the valence angles about the germanium atom should alter from the tetrahedral angle of 109.5° toward the theoretical values for either a trigonal bypyramid or an octahedron, as the coordination number increases from four, through five, to six. Microwave data for gaseous trimethylcyanogermane provide comparative molecular parameters for the free molecule (*66*), although the critical $H_3C—Ge—CH_3$ angle is omitted in the report.

In the extreme case in which the cyanide groups lie midway between adjacent germanium atoms in $(CH_3)_3GeCN$, the geometry about the central atom would be that of a trigonal bipyramid in which the two axial sites are occupied by the more electronegative $C{\equiv}N$ moieties. Such a situation is exemplified in $(CH_3)_3SnCN$ (*151*), where the C—Sn—C angle is 120°, and any tendency toward this structure in the germanium compound should be reflected in a C—Ge—C angle intermediate between the tetrahedral (109.5°) and trigonal bipyramidal (120°) extremes. The observed $H_3C—Ge—CH_3$ angles in $(CH_3)_3GeCN$ are 114.1 and 116.2°, which, although in excess of 109.5°, do not alone provide confirmation of a bridged structure, because even in the free molecule this angle should expand slightly from tetrahedral solely on the grounds of isovalent rehybridization (*16*). However, in conjunction with the $H_3C—Ge—CN$ angles (103.0, 104.2°) which have closed from 106.2° in the gas phase toward the 90° expected in a regular trigonal bipyramidal structure, and in the light of the molecular packing which brings components of the intermolecular coordinate bond into juxtaposition, the long N: → Ge interaction can be taken as real.

Valence angles in $(CH_3)_2Ge(CN)_2$ show even more marked deviations from the gas phase values, again confirming the long, intermolecular N: → Ge bonds (*112*). For example, the $H_3C—Ge—CH_3$ angle (120.9°) is distorted toward 180°, the value expected for a *trans*-R_2GeX_4 octahedron, the geometry most prevalent in diorganotin chemistry (*49, 185*), and the structure toward which the analogous $(CH_3)_2Sn(CN)_2$ distorts (*112*).

4. *Carborane Derivatives*

While isovalent rehybridization to provide a greater *p*-content to bonds involving more electronegative atoms or groups at the expense of more electropositive ones (*16*) is now well accepted, exceptions can occur when steric factors outweigh electronic ones. Thus, in bis(*o*-carboranyl)dimethylgermane (*10*) the tetrahedral angles at germanium are expanded for both the $H_3C—Ge—CH_3$ residue (114.2°) and the angle involving the more electronegative cage ligands [C(carb)—Ge—C(carb) = 112.6°]. This latter angle is reduced to 108.4° in **5** where the two carborane ligands are linked via a phosphorus atom bonded to each of the second carbon atoms in the cage (*24*).



(5)

The six-membered heterocycle central to **5** does not adopt the boat conformation shown by the related anthracenyl derivatives discussed earlier (see Section III,B,2); rather the GeC_4 moiety is coplanar, with the phosphorus atom lying 0.33 Å out of this plane in an envelope arrangement reminiscent of $(CH_3)_3GeC_5H_5$ (*173*). The structure of $HCB_{10}H_{10}CGe(CH_3)_3$ has also been determined.

C. Polyorganogermanes

The tendency toward catenation for the carbon group elements decreases as atomic radius increases, that is, as M—M bond energies decrease. The structural chemistry of organometallic compounds of this group, which contain the $(M—M)_n$ unit, ranges from copious in the case of silicon (*128*) to almost nonexistent in the case of lead, passing through a group of polyorganotins dominated by short chain, ditin compounds (*49, 185*). The structural data for polyorganogermanes appropriately attests to their position in this stability sequence, and in addition to the simple digermanes (*54, 55*) a linear tetragermane (*58*) and cyclic species containing four (*146–148*) and six (*56, 57, 97*) germanium atom chains have been studied.

Hexaphenyldigermane can be isolated from chlorinated hydrocarbon solvents in both triclinic and metastable hexagonal modifications, whereas from benzene a rhombohedral modification incorporating eight solvent molecules crystallizes. The structures of the triclinic (*54*) and rhombohedral (*55*) modifications have been determined, and yield Ge—Ge bond lengths of 2.437 and 2.445 Å, respectively. In each case the two $(C_6H_5)_3Ge$ units adopt an achiral bipropeller conformation with respect to each other, the gross conformation of the solvated modification seemingly unaffected by the presence of two benzene molecules sandwiching the Ge—Ge bond (*55*).

Not surprisingly, a completely staggered conformation is maintained in the symmetrical, linear, terminally substituted diiodidooc-

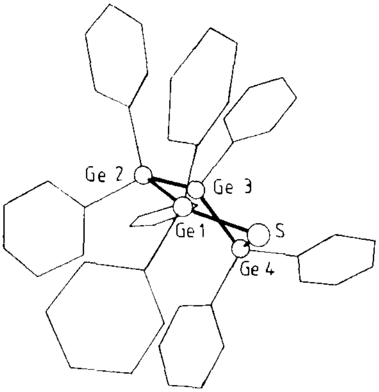


FIG. 7. The structure of $[(C_6H_5)_2Ge]_4S$ showing the envelope conformation of the heterocyclic ring.

taphenyltetragermane (*58*), with the two iodine atoms disposed in a trans arrangement as dictated by the center of symmetry at the midpoint of the central Ge—Ge bond.

A Ge_4 polygermane ring has also been studied (cf. Addendum for a Ge_3 ring). The intraring Ge—Ge bond lengths (mean value 2.465 Å) in octaphenyl cyclotetragermane (*147*) are equal within experimental error to those in the linear iodinated compound (2.451, 2.459 Å) (*58*), and are sufficiently long to form a nearly distortion-free, planar (angle of pucker = 3.9°), square (range ∠Ge—Ge—Ge = 90.2–89.4°), four-membered ring of approximately D_{2d} geometry (*147*). Shorter intraring bond distances in cyclobutane, and the cyclotetrasilanes $[(C_6H_5)_2Si]_4$ and $[(CH_3)(t\text{-}C_4H_9)Si]_4$ all exhibit major distortions from ring planarity [angle of pucker = 20–40° (*130*), 12.8° (*138*), and 36.8° (*96*), respectively]. No cyclic tetrastannanes $[R_2Sn]_4$ are available for comparison (*49, 185*).

The Ge_4 moiety is also incorporated into two five-membered heterocycles, $(C_6H_5)_8Ge_4X$, X = S (*146*), Se (*148*). The ring in the sulfur compound adopts an envelope configuration (Fig. 7), with Ge(4) lying almost 1 Å out of the plane of the remaining atoms (*146*). In contrast, the corresponding selenium compound is almost perfectly planar, the maximum deviation from the ring plane being only 0.14 Å (*148*).

The largest polyorganogermanes studied structurally to date are based upon cyclohexagermane. Two different solvates of $[(C_6H_5)_2Ge]_6$, containing either seven benzene (*57*) or two toluene (*56*) molecules in the crystal, are known and can be compared to the solvent-free dodecamethyl analog (*97*). In all three compounds the ring formed by the six

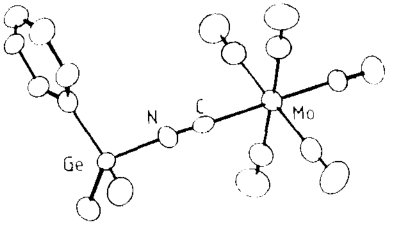


FIG. 8. The molecular structure of $(CH_3)_2C_6H_5GeNCMo(CO)_5$.

germanium atoms adopts a chair configuration with the expected six axial and six equatorial hydrocarbon substituents.

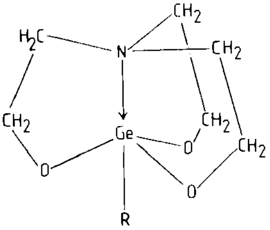
The presence of seven benzene molecules in the clefts between germanocycles brings about a flattening of the Ge_6 chair (*57*) and this distortion is accentuated in the toluene solvate in which the two $C_6H_5CH_3$ molecules sandwich the distorted plane of the Ge_6 ring (*56*) in an arrangement similar to that in $(C_6H_5)_6Ge_2 \cdot 2C_6H_6$ (*55*). Relative to dodecamethylcyclohexagermane (*97*), the two solvated dodecaphenyl analogs show a lengthening of the Ge—Ge bond from 2.374 (*97*) to 2.457 Å for the benzene (*57*) and still further to 2.463 Å for the toluene solvate (*56*) where most disruption of the germanocycle geometry is incurred. Dodecamethylcyclohexagermane is isostructural with its silicon analog (*39*), whereas $[(C_6H_5)_2Sn]_6$ also adopts a chair conformation (*137*).

IV. Group VA Derivatives

The bonds formed between germanium and elements of Group VA can be divided into two categories: those in which the element is bonded via a covalent bond and others in which a Lewis acid–Lewis base interaction between the two elements results in coordinate bond formation. The same classification of bond types is also appropriate when discussing organogermanium derivatives of Groups VIA and VIIA.

Both triphenylgermanium isocyanate (*159*) and dimethylphenylgermanium isocyanide (pentacarbonyl)molybdenum (*166*) (Fig. 8) are simple, tetrahedral molecules, in which nitrogen is covalently bonded to germanium at distances of 1.83 and 1.897 Å, respectively. Isovalent rehybridization (*16*) at germanium to accommodate a greater *p*-content in the bonds to the more electronegative nitrogen in each case reduces the C—Ge—N angles below 109.5°, while simultaneously expanding C—Ge—C angles in accord with a greater *s*-component of the Ge—C bonds (*159, 166*). The lattice arrangement of $(C_6H_5)_3GeNCO$ shows no molecular ordering, unlike the corresponding tin compound which forms polymeric chains of planar $[(C_6H_5)_3Sn]$ groups linked by NCO bridges (*158*).

For comparison, a number of compounds incorporating coordinate N: → Ge bonds have been reported, among which studies of organogermatranes (**6**) by several Russian authors (*12, 18, 77, 87, 104, 105, 180*) predominate.



(6)

In the three germatranes $[RGe(OCH_2CH_2)_3N$, R = ethyl (*12*), iodomethyl (*87*), or α-naphthyl (*105*)] and the related compound $C_6H_5Ge[(OCH_2CH_2)_2(O_2CCH_2)]N$ (*77*) for which complete structure analyses were performed, the germanium occupies the center of a distorted trigonal bipyramid flanked by three oxygen atoms in the equatorial positions with the nitrogen and the R group disposed in a trans manner in the axial sites. The N: → Ge bonds are in the range 2.19–2.24 Å, in excess of both the theoretical (1.92 Å) and experimental (*vide supra*) covalent bond lengths, but considerably shorter than the sum of the van der Waals radii.[2] They are also significantly less than the analogous bridging bond in $(CH_3)_3GeCN$ [3.57 Å (*152;* see Section III,B,3)], behavior which is attributable to both the spatial constraints imposed upon the nitrogen by the triply chelating ligand and the increased Lewis acidity of a germanium bonded to three oxygens and carbon rather than four carbon atoms. The angles at germanium, which are ~96 and 82° for the C—Ge—O and N—Ge—O angles, respectively (*12, 87, 105*), describe the transition between tetrahedral and trigonal bipyramidal geometries with concomitent approach of the axial nitrogen, a situation which has recently been described (*30*) in terms of positions along the pathway of an SN2 displacement reaction.

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[2] Quoted as 3.8 Å in Refs. (*12*) and (*26*), based upon an estimated van der Waals radius for germanium of 2.3 Å. Other authors (*112;* see Section III,B,3) approximate the Ge ··· N van der Waals contact distance to the lower value of 3.5 Å by analogy with As ··· N contacts.

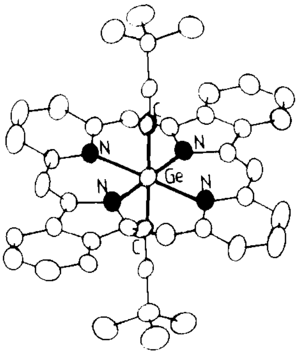


FIG. 9. The structure of bis(3,3-dimethyl-1-butyneyl)hemiporphyrazine germanium, showing the octahedral geometry about the metalloid.

Five-coordination at germanium is also achieved via chelation in *o*-$[(CH_3)_2NCH_2]C_6H_4Ge(CH_3)(C_6H_5)Cl$ (*28;* see Section VI), and again the trigonal bipyramidal geometry, which also dominates the chemistry of this coordination number for tin, is adopted. In comparison with the germatranes, the coordinate bond (Ge—N: 2.479 Å) is somewhat longer, while the relative geometric flexibility of the singly chelating ligand allows the two most electronegative atoms to occupy the favored axial sites.

The constraints of the tetradentate hemiporphyrazine ligand impose a six-coordinated *trans*-R_2GeN_4 octahedral geometry (Fig. 9) on bis(3,3-dimethyl-1-butyneyl)hemiporphyrazinogermanium, in which both covalent (1.956 Å) and coordinate (2.172 Å) Ge—N bonds are incorporated (*92*). The heterocycle is nearly planar, and this structure represents the only unequivocal example of a six-coordinated organogermane whose structure is known thus far.

Instances of an R_nGe—P bond are confined to one example, the adamantane-like cage compound, $[(CH_3)_3Ge]_6P_4$ (*51*). The Ge—P distance (2.3217 Å) is equal to the sum of covalent radii (2.32 Å), although the strained trifurcated bonding of each phosphorus atom (Fig. 10) suggests that this may not be representative of a "typical" covalent Ge—P bond. Such speculation awaits further study for confirmation.

Cage structures also prevail in two organogermanium–bismuth compounds $[(C_6F_5)_2Ge]_3Bi_2$ and $[(C_6F_5)_2Ge]_3Bi_2Pt[P(C_6H_5)_3]_2$ (*19*). The former, surprisingly the product of the reaction between $(C_6F_5)_2GeH_2$ and $Bi(C_2H_5)_3$, forms a trigonal bipyramidal heteroelemental framework (Fig. 11) in which apical bismuth atoms are linked by organogermyl bridges. The average values of the six Ge—Bi bonds is 2.739 Å

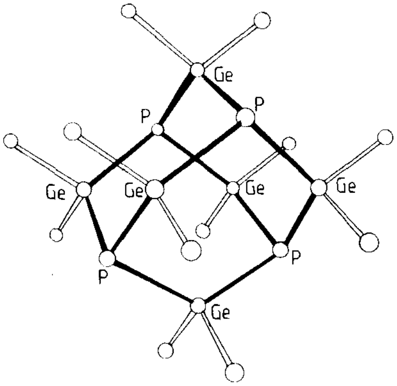


FIG. 10. The structure of $[(CH_3)_2Ge]_6P_4$, emphasizing the adamantane-like cage arrangement of germanium and phosphorus atoms.

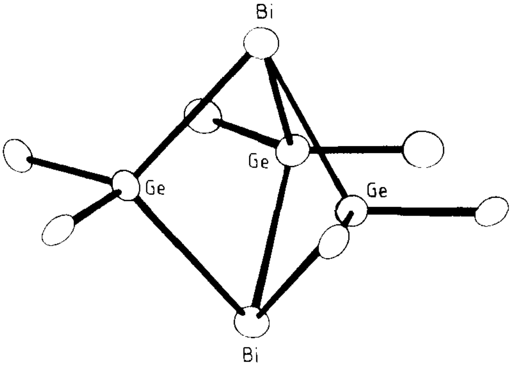


FIG. 11. The heteroelement framework of $[(C_6F_5)_2Ge]_3Bi_2$. Only the α-carbon of the perfluorophenyl groups is included for simplicity.

(*19*). The geometry approximates tetrahedral at the metalloid and pyramidal at the metal, although the interatomic angles deviate significantly from the ideal. When reacted with $[(C_6H_5)_3P]_3Pt$, the transition metal inserts into one of the Ge—Bi bonds to yield a six-atom heterocyclic cluster, $[(C_6F_5)_2Ge]_3Bi_2Pt[P(C_6H_5)_3]_2$ (Fig. 12).

The two bismuth atoms in the molecule are bridged by two $(C_6F_5)_2Ge$ and one $(C_6F_5)_2GePt[P(C_6H_5)_3]_2$ moiety, i.e., the framework has two five-membered and one four-membered heterocycles (*19*). The two five-membered rings show an envelope conformation, with fold angles along the Bi-1 ··· Bi-2 line of 60.3° toward Ge-2 and 66.6° toward Ge-3. The Ge—Bi bonds range in length from 2.695 to 2.774 Å, with the Ge—Pt bond equal to 2.466 Å (cf. Section VII).

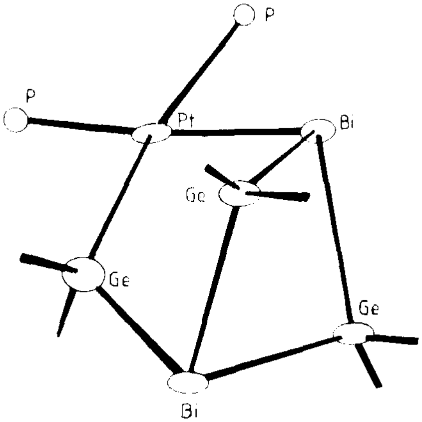


FIG. 12. The heteroelement framework of $[(C_6F_5)_2Ge]_3Bi_2Pt[(P(C_6H_5)_3]_2$. The aromatic groups have been omitted for clarity.

V. Group VIA Derivatives

Interest in the ether derivatives of the lower elements of Group IVA has centered on the rationalization of the M—O—M angle with respect to both M—O and M ··· M contacts and the relative size of the organic substituents on M. Despite the abundance of data available for correlation, no systematic trend seems to have emerged (Table IV). For example, hexaphenyldigermoxane, $(C_6H_5)_3GeOGe(C_6H_5)_3$, is bent [∠Ge—O—Ge = 135.2 (*79*); 137° (*115*)], as is the corresponding stannoxane [∠Sn—O—Sn = 137° (*82*)], whereas the siloxane analog is perfectly linear at oxygen by the demands of symmetry (*80*). These observations suggest that angular variations at oxygen are a function of the M—O internuclear separation, a postulate supported by the bent structure of $(C_6H_5)_3EOM(C_6H_5)_3$ [E = Si, M = Ge, E = Si, M = Sn, and E = Ge, M = Sn (*131*)], but completely at variance with the carbonoid hexaphenyl ether which is most acute [∠C—O—C = 127.9° (*81*)] despite incorporating the shortest M—O bond [1.454 Å (*81*)]. Similarly, while the increased bulk of the benzyl relative to the phenyl group might be expected to be offset by its increased flexibility (via rotation at both the methylene and α ring carbons), both $[(C_6H_5CH_2)_3M]_2O$ [M = Ge (Fig. 13) and Sn] are unexpectedly linear at oxygen (*83, 84*). Despite the differences in bulk of the group bonded to germanium, both hexamethyldigermoxane (*177*) and $[\eta^5\text{-}C_5H_5)(CO)_2\text{-}FeGe(CH_3)_2]_2O$ (*2*) have similar angles at the bridging oxygen (Table IV).

TABLE IV

SELECTED Ge—X (X = O,S,Se) INTERNUCLEAR DISTANCES (Å) AND ANGLES (DEGREE)[a]

Compound	Ge—O	Ge—S	Ge—Se	Ge—E—Ge	Reference
$[(C_6H_5)_3Ge]_2O$	1.767[b]			135.2	*79*
	1.75[b]			137	*115*
$(C_6H_5)_3GeOSi(C_6H_5)_3$	1.711[c]			142.5	*131*
$(C_6H_5)_3GeOSn(C_6H_5)_3$	1.862[c]			134.9	*131*
$[(C_6H_5CH_2)Ge]_2O$	1.730			180	*83, 84*
$[(CH_3)_3Ge]_2O$	1.77[b,d]			141	*177*
$[(C_5H_5)(CO)_2FeGe(CH_3)_2]_2O$	1.785[b]			134	*2*
$[H_3Ge]_2O$	1.767[b,d]			126.5	*85*
$R_2Ge(H)(OC_2H_5)$[e]	1.797				*118*
$R_2Ge(OH)(C_6H_5)_2$[f]	1.838				*78*
$[(C_6H_5)_3Ge]_2S$		2.235[b]		111.0	*113*
$(C_6H_5)_3GeS(t\text{-}C_4H_9)$		2.229			*47*
$[(CH_3)_3Ge]_2SW(CO)_5$		2.264 2.283			*140*
$(CH_3Ge)_4S_6$		2.218[b]			*15*
Cyclo-$[(C_6H_5)_2Ge]_4S$		2.240[b]			*146*
Cyclo-$[(C_6H_5)_2Ge]_4Se$			2.373(1)		*148*

[a] X-Ray crystallographic data, unless indicated otherwise.

[b] Mean Ge—E distance.

[c] Occupancy weighted mean of the Ge—O and M—O distances.

[d] Electron-diffraction data.

[e] R = $[(CH_3)_3Si]_2CH_2$—.

[f] R = $(C_6H_5)[(C_2H_5)_3P]_2Pt$—.

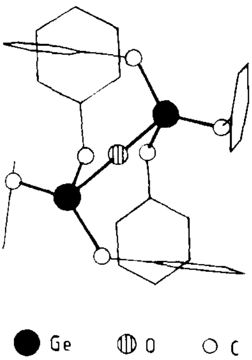
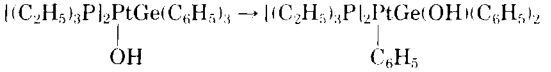


FIG. 13. The molecule of $[(C_6H_5CH_2)_3Ge]_2O$. The Ge—O—Ge fragment is linear, and the organic groups adopt a staggered conformation.

One consistent feature of all these ethers is the disordered nature of the crystals. This manifests itself in rotameric disorder (*2*), site disorder for the lower Group IVA elements in R_3MOER_3 ($M \neq E$) (*131*), and disorder owing to the presence of a mixed crystal originating from impure starting materials in synthesis (*83*). In related compounds, two conformers of $[(C_6H_5)_3Ge]_2S$ have been isolated and characterized, and differ only with respect to a rotation of $(C_6H_5)_3Ge$ groups about the Ge—S bonds (*113*). Site disorder also occurs in the peroxide $(C_6H_5)_3GeOOSi(C_6H_5)_3$ (*121*), so that the M—O internuclear distance (1.742 Å) merely reflects an occupancy weighted average of the two distinct M—O bonds, as it does with the mixed element ethers discussed above.

Of the remaining structures containing covalent Ge—O bonds, the structures of a number of five-coordinated germatranes, $RGe(OCH\text{-}CH_2)_3N$, in which the three oxygen atoms occupy the equatorial sites in the trigonal bipyramid about germanium (range Ge—O = 1.69–1.81 Å) have been previously discussed (see Section IV). Two other derivatives have been reported which incorporate either a Ge—OH (*78*) or $Ge—OC_2H_5$ (*118*) moiety, although both are more notable for the preparative rather than their structural chemistry. The synthesis of the latter, involving oxidative addition of $\{[(CH_3)_3Si]_2CH\}_2Ge(II)$ across the O—H bond of ethanol, has already been discussed (see Section II). The Ge—OH bond in *cis*-$[(OH)(C_6H_5)_2Ge](C_6H_5)Pt[P(C_2H_5)_3]_2$ arises from internal rearrangement of the isomeric triphenylgermylhydroxyplatinum compound (*78*):



$$[(C_2H_5)_3P]_2\underset{\displaystyle OH}{\underset{|}{Pt}}Ge(C_6H_5)_3 \rightarrow [(C_2H_5)_3P]_2\underset{\displaystyle C_6H_5}{\underset{|}{Pt}}Ge(OH)(C_6H_5)_2 \qquad (1)$$

Unique not only among the germanium–oxygen compounds but in the whole field of structural organogermanium chemistry is the lattice structure of carboxyethylgermanium sesquisoxide, $O_3(GeCH_2CH_2\text{-}COOH)_2$ (*168*). An infinite sheet arrangement is formed (Fig. 14), made up of interlinked 12-membered rings. Each basic ring unit is comprised of six germanium-centered tetrahedra bridged by six oxygen atoms in an alternating array. Carboxylate chains alternate above and below these infinite sheets, and a network of hydrogen bonds between carboxyl groups of adjacent sheets extends the polymer to a third dimension. The similarity between the 12-membered ring at the heart of this structure and the crown ethers may account for its reported biological activity (*169*).

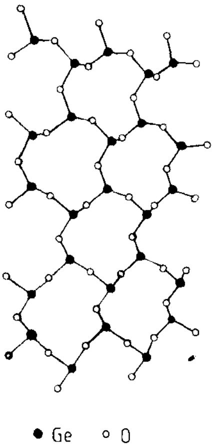
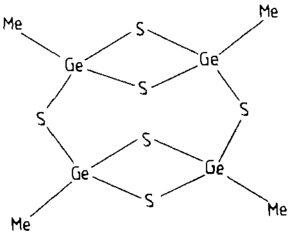


FIG. 14. A portion of the layer network of $O_3(GeCH_2CH_2CO_2H)$. The alkyl carboxylate groups, which have been omitted for clarity, alternate above and below the polymeric sheet.

In addition to $[(C_6H_5)_3Ge]_2S$ (*113*), four other organogermanium–sulfur compounds have been investigated, including the cyclic octaphenyltetragermanium sulfide (*146*) discussed in Section III,C. Triphenylgermanium-*p*-*t*-butylphenylmercaptan (*47*) and tetra(methylgermanium)hexasulfide (*15*) are both isostructural with their organotin counterparts (*43* and *111*, respectively), the former a distorted tetrahedron in geometry while the latter adopts an adamantane-like cage structure (cf. Fig. 10) rather than the open cage (**7**).



(7)

Bis(trimethylgermyl)sulfide has been coordinated to tungsten pentacarbonyl, and its structure determined (*140*).

Three structures containing $R_nGe—Se$ bonds are known (*148*), namely cyclo-Ph_8Ge_4Se (Ge—Se: 2.373 Å), the six-membered ring $(Ph_2GeSe)_3$ (2.342–2.363 Å), and the adamantyl $(PhGe)_4Se_6$ (2.339–2.360 Å).

TABLE V

SELECTED GERMANIUM–HALOGEN BOND LENGTHS (Å)

Compound	Ge—F	Ge—Cl	Ge—Br	Ge—I	Ge—C	Reference
CH_3GeF_3[a]	1.714				1.904	*59*
$(CH_3)_2GeF_2$[a]	1.739				1.928	*59*
$(CH_3)H_2GeF$[b]	1.751				1.925	*145*
Cl_3CGeCl_3[a]		2.111				*171*
CH_3GeCl_3[b]		2.135				*63*
$(CH_3)_3GeCl$[b]		2.170			1.940	*64*
CH_3GeBr_3[a]			2.276		1.89	*60*
$(CH_3)_2GeBr_2$[a]			2.303		1.91	*60*
$(CH_3)_3GeBr$[b]			2.323		1.936	*122*
$(C_6H_5)_3GeBr$[c]			2.320		1.935	*144*
$I[(C_6H_5)_2Ge]_4I$[c]				2.559(1)	1.949	*58*

[a] Electron-diffraction data.

[b] Microwave spectroscopic data.

[c] X-Ray crystallographic data.

VI. Group VII Derivatives

As with the volatile organogermanium hydrides (Section II), the structural chemistry of the simple organogermanium halides is dominated by microwave and electron diffraction studies. In both the gaseous and solid states these species are invariably tetrahedral (although often of varying degrees of irregularity), and only in cases in which an additional bridging or chelating group other than the halide is present does the coordination sphere expand to accommodate five bonds to the central atom. Such behavior is in direct contrast to the chemistry of tin and lead, where the formation of associated lattices via halide bridges is common, if not the norm (*49, 143, 185*).

Despite the mundane nature of the their molecular geometries, a number of interesting trends in both bond lengths and angles are discernible (Table V).

For all three lightest halides, both the Ge—X (X = F, Cl, Br) and (availability of data permitting) Ge—C bond lengths show a decreasing trend with increasing halogen substitution. For example, in $(CH_3)_nGeBr_{4-n}$, the Ge—X bond length changes from 2.323 (*122*) to 2.303 to 2.276 Å (*60*) as n decreases from 3 to 2 and finally to 1. Simultaneously, the Ge—C bond decreases in length in the order 1.936 (*122*), 1.91, 1.89 Å (*60*) for the same sequential variation in n. Two apparently contradictory descriptions of the bonding in these compounds are capable of rationalizing this behavior (*59*). On simple rehybridization arguments (*16*), increasing the number of methyl groups on germanium, each of which prefers *s*-dominated hybrid orbitals centered on the latter for bonding, enhances the *p*-content of the hybrid orbitals involved in bonding to the halogen, hence lengthening the Ge—X bond. Lengthening of the Ge—C bond with increasing methylation occurs simply because the available *s*-character in these bonds is spread more thinly. Conversely, on bond polarity grounds, the electron content of the Ge—C bonds exceeds that of the Ge—X bonds, although this difference diminishes as the germanium undergoes increasing halogenation. While such a scenario leads qualitatively to the same results as the rehybridization model, it invokes the contradictory assumption that sp^3 hybridization is maintained at germanium for all the compounds considered (*59*). Both descriptions are also capable of satisfactorily explaining the variations in bond angles, which for any compound follow the general order $\angle$C—Ge—C $\gg$ X—Ge—C $\approx$ X—Ge—X. For example, the relevant angles for $(CH_3)_2GeBr_2$ are 124, 107, and 104°, respectively (*60*).

The only reports of an organogermanium–iodine bond occur in the polygermane, $I[(C_6H_5)_2Ge]_4I$ (*58;* see Section III,C) and the cyclic 1,4-digermacyclohexadiene, $I_2GeC_4H_4GeI_2$ (*21, 178*). The two reports offer Ge—I distances of 2.559 (*21*) and 2.48 Å (*178*), respectively.

Products of the reaction between germanium(II) halides and —C≡C— triple bonds, of which the above diiodide is but one, have been exhaustively reported by a number of Russian workers (*21, 23, 175, 176, 178, 179*). In contrast to the dimeric structure (**3**) shown by the iodinated compound in the solid (*178*), the structure in the gaseous phase revealed by an electron diffraction study (*176*) is volatilization-temperature dependent with both monomeric (**2**) and dimeric (**3**) products observed. The corresponding product from reaction of $GeCl_2$ with $C_6H_5C{\equiv}CC_6H_5$ forms the six-membered ring structure in both phases (*21, 175*). The composition of the tetraorganogermanes obtained by alkylation or arylation of these halogenated species and the significance of $(p \rightarrow d)$-π bonding in the class as a whole is discussed in Section III,B,2.

Other cyclic organogermanes have aroused interest because of the possibility of $(p \rightarrow d)$-π bonding between germanium and the ring atoms, particularly when the other ring atoms are components of an aromatic species. The structure of 10,10-dichloro-10-germa-9-oxa-9,10-dihydroanthracene (*170*) is discussed in this context in Section III,B,2.

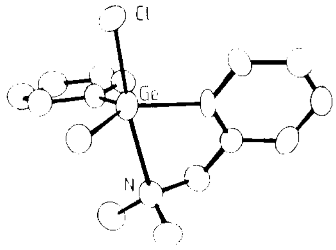


FIG. 15. The molecular structure of o-[$(CH_3)_2NCH_2]C_6H_4Ge(CH_3)(C_6H_5)Cl$.

Apart from π bonding possibilities within the ring, interest has also centered on conformational aspects of the structures of cyclic organogermanes. 2,2,4,4-Tetrachloro-1,3-bis(trimethylsilyl)-2,4-digermacyclobutane (*88*) forms part of a series of studies in which cyclobutane is substituted by heteroatoms in the 1,3 positions. The conformation of four-membered rings appears to be a compromise between two opposing factors: minimization of either the van der Waals repulsions between diagonally opposite atoms on the one hand or the intraring twisting stress on the other (*88*). As cyclobutane is substituted by heteroatoms from Group IVA in the 1,3 positions, the increasing ease of internal rotation about the C—M bond (M = Si,Ge) should encourage ring planarity. Such a trend, indicated by reduction in the ring-folding angle from ~30° in cyclobutane (**3**) to 14° in 1,3-(dichlorosilyl)cyclobutane (**4**), is further endorsed by an almost planar ring (fold angle = 0.6°) in the halogenated, cyclic organogermane (*88*).

Five-coordinated organogermanium halides arise only when a second, bifunctional group is bonded to the germanium. The molecular structure of o-$(CH_3)_2NCH_2C_6H_4Ge(CH_3)(C_6H_5)Cl$ (*28;* see Section IV) reveals that the o-substituted phenyl group is bidentate, and the presence of the electron-withdrawing chlorine confers sufficient Lewis acidity on the germanium to promote N: → Ge coordinate bond formation. The more electronegative nitrogen and chlorine atoms occupy the apical positions in trigonal bipyramidal arrangement of bonds about the metalloid (Fig. 15), with the result that the Ge—Cl bond length (2.327, 2.301 Å for the two crystallographically independent molecules in the asymmetric unit) is the longest so far reported.

1-Substituted 2,3,4,5-tetraphenylgermacyclopentadienes have been utilized as π-donor ligands toward $Fe(CO)_3$, via the 2,4-butadiene part of the germanocycle. The structure of one member of this series, the 1-fluoro-1-methyl-derivative (Fig. 16), has been elucidated (*98*) and presents an interesting comparison with 1,1-diethylnyl-2,3,4,5-tet-

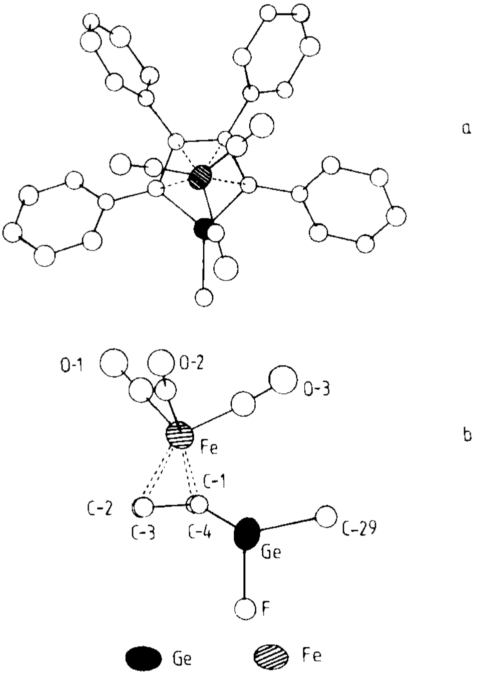


FIG. 16. Views of tricarbonyl(1-*exo*-fluoro-1-methyl-2,3,4,5-tetraphenyl-1-germacyclopentadienyl)iron, (a) perpendicular to the C_4Ge plane and (b) perpendicular to the Fe ring interaction (phenyl groups omitted for clarity).

raphenylgermacyclopentadiene (*125;* see Section III,B,2), an analog of the free parent germacyclopentadiene. Complexation induces greater distortions in the planarity of the five-membered ring, the germanium moving from ~0.1 Å out of the C_4 plane in the tetraorganogermane (*125*) to a 1 Å displacement in the transition metal complex. This represents a change in the ring envelope angle [i.e., folding along C-1 ··· C-4] from ~4 to 31.1°. The alternating arrangement of C—C single and double bonds within the ring of the ethynyl derivative (see Section III,B,2) gives way to a completely conjugated C_4 chain when complexed with $Fe(CO)_3$ and three equal C—C bonds [1.44 Å (*98*)] interim in length to the localized bonds of differing order [~1.35 and 1.51 Å (*125*)] in the free heterocycle.

Organogermanium chlorides have also been utilized as ligands in a number of organoiron complexes (*7, 8, 35*) and the structures of these compounds are discussed in the context of the Ge—Fe bond (see Section VII).

VII. Transition Metal Derivatives

Compounds in which an organogermane is bonded to a transition element (including Group IIB) by a direct metalloid–metal bond have been structurally characterized for manganese (*37, 108, 157, 167*), iron (*1, 2, 7, 8, 33, 35, 48, 53, 70, 71, 184*), cobalt (*13, 38, 50, 155*), nickel (*163*), cadmium (*163*), molybdenum (*40*), chromium (*119*), ruthenium (*32, 93, 94*), rhenium (*157, 181*), platinum (*19, 78*), and mercury (*116, 117, 164*). These species can be loosely classified into four structural types: linear, triangular, square, and trigonal bipyramidal clusters (Table VI). The general area of germanium transition metal chemistry has been the subject of recent reviews (*44, 134*).

Of the linear clusters, the organogermanium-substituted transition metal carbonyl compounds are the simplest. In every case, the coordination at germanium is tetrahedral, while the transition element retains the geometry of the parent carbonyl compound (*50, 108, 119, 155, 157, 181*). The Ge—M bond is almost without exception shorter than the sum of the Ge—M covalent radii (Table VI), which is cited as evidence for $(d \rightarrow d)$-π multiple bonding.

The shortest Ge—Fe bond reported to date [2.28 Å (*7, 8*)] occurs in $(\eta^5\text{-}C_5H_5)(\eta^4\text{-}C_4H_6)FeGe(CH_3)Cl_2$ (Fig. 17), and is attributed to a strong $[d(Fe) \rightarrow d(Ge)]$-$\pi$ back-donation, promoted by the weak π-acceptor ligands (C_5H_5, C_4H_6) on iron and the electronegative halogen atoms bonded to germanium (*7, 8*).

The rhenium derivative $(CH_3)_3GeRe(CO)_5$ can be converted into the carbene complex $(CH_3)_2\overline{GeRe(CO)_4C(O}){CH_3}$, which in solution is in equilibrium with its dimer. The dimer crystallizes preferentially, and incorporates an eight-membered $[GeReCO]_2$ heterocycle (*181*).

The nearly linear Ge—Ru—Ru—Ge spine in the organoruthenium complex $Ru_2[Ge(CH_3)_3]_2(CO)_4(C_8H_6)$ has provided a basis for the first example of a stable eight-electron pentalene ligand (*32, 94*). The two carbon atoms common to both hydrocarbon rings [C-4—C-8, Fig. 18] are bonded to both ruthenium atoms in the form of a transverse bridge, the remaining two groups of three carbon atoms of the pentalene ligand bonding each as η^3-allyl interannular units to one ruthenium atom.

The structure of $(C_6H_5)_3GeMo(CO)_2(\eta^5\text{-}C_5H_5)C(OC_2H_5)C_6H_5$ has a trans arrangement of ligands about the molybdenum (*40*). Related carbene structures that have been determined are the optically active *cis*-S-$(CH_3)(C_6H_5)(C_{10}H_7)GeMn(CO)C(OC_2H_5)CH_3$ (*37*), $(C_6H_5)_3GeCo(CO)_3C(OC_2H_5)C_2H_5$ (*38*), and the dimeric rhenium complex (*181*) discussed above.

TABLE VI

TRANSITION METAL DERIVATIVES

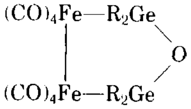
Compound	Type[a]	Ge—M (Å)	Sum Ge—M covalent radii (Å)[b]	M—M (Å)	Reference
M = Mn			2.57		
$Ph_3GeMn(CO)_5$	Linear	2.53, 2.54[c] 2.60[d]			*108* *157*
$Me(C_{10}H_7)PhGeMn(CO)[C(OEt)Me]$	Linear	2.524			*37*
$Me_2GeMn_2(CO)_9$	Triangular	2.477, 2.432		2.854	*167*
M = Fe			2.52		
$[Me_2GeFe(CO)_2(cp)]_2O$	Linear	2.372			*2*
$MeCl_2GeFe(C_4H_6)(cp)$	Linear	2.28, 2.29			*7, 8*
	Linear	2.876			*53*
$[ClCH_2SiMe_2CH_2]ClGeFe_2(CO)_8$	Triangular	2.375		2.814	*35*
$Me_2GeFe_2(CO)_3(\eta^5\text{-}Cp)_2$	Triangular	2.347, 2.345		2.628	*1*
$Ph(Ph_4C_4H)GeFe_2(CO)_8$	Triangular	2.408, 2.430		2.785	*48*
$[(ClCH_2SiMe_2CH_2)ClGeFe(CO)_4]_2$	Square	2.445, 2.443			*35*
$[Et_2GeFe(CO)_4]_2$	Square	2.492			*184*
$(Me_2Ge)_3Fe_2(CO)_6$	tbp	2.398(4)		2.750	*33, 71*
$(Ph_2Ge)_2Fe_2(CO)_7$	tbp[e]	2.402–2.440		2.666	*70*
M = Co			2.56		
$Ph_3GeCo(CO)_3(PPh_3)$	Linear	2.34			*155*
$Ph(C_{10}H_7)MeGeCo(CO)_4$	Linear	2.458			*50*
$Ph_3GeCo(CO)_3[C(OEt)Et]$	Linear	2.419			*38*
$PhGeCo_3(CO)_{11}$	Triangular	2.375, 2.392[f]		2.546	*13*
M = Cr					
$[(Me_3Si)_2CH]_2GeCr(CO)_5$	Linear	2.406			*119*
M = Mo					
$Ph_3GeMo(\eta^5\text{-}Cp)(CO)_2[C(OEt)Ph]$	Linear	2.658			*40*
M = Ru					
$(Me_3Ge)_2Ru_2(CO)_4(C_8H_6)$	Linear	2.476–2.491		3.056, 3.060	*32, 95*
$[Me_2GeRu(CO)_3]_3$	Triangular	2.482, 2.500		2.926	*93, 94*

TABLE VI (*continued*)

Compound	Type[a]	Ge—M (Å)	Sum Ge—M covalent radii (Å)[b]	M—M (Å)	Reference
M = Re			2.58		
$Me_3GeRe(CO)_5$	Linear	2.69			*157*
$[Me_2GeRe(CO)_4C(O)Me]_2$	Linear	2.591			*181*
M = Pt			2.53		
$Ph_2(OH)GePtPh(PPh_3)_2$	Linear	2.433			*78*
$[(C_6F_5)_2Ge]_3Bi_2Pt(PPh_3)_2$	tbp[g]	2.466			*19*
M = Hg			2.52		
$(Ph_3Ge)_2Hg$	Linear	2.543, 2.514			*164*
$[(C_6F_5)_3Ge]_2Hg$	Linear	2.483			*117*
$(C_6F_5)_3GeHgPt(PPh_3)_2Sn(C_6F_5)_3$	Linear	2.534			*116*
M = Ni			2.35		
$[(Ph_3GeCd)(\eta^5\text{-}Cp)(Ph_3Ge)Ni]_2Cd$	Linear	2.308			*163*
M = Cd			2.60		
$[(Ph_3GeCd)(\eta^5\text{-}Cp)(Ph_3Ge)Ni]_2Cd$	Linear	2.587			*163*

[a] tbp, Trigonal bipyramid.

[b] Ref. (*139*).

[c] Space group = $P1$.

[d] Space group = $A2/a$.

[e] One site on the tbp is occupied by a bridging CO group.

[f] An additional Ge—Co bond [2.456(3) Å] is exocyclic to the triangular $GeCo_2$ cluster.

[g] One site on the tbp is occupied by the $(C_6F_5)_2GePt[P(C_6H_5)_3]_2$ moiety to yield a tricyclic cluster.

Three linear organogermanium mercury structures have been reported (*116, 117, 164*). The two independent molecules in the asymmetric unit of $[(C_6H_5)_3Ge]_2Hg$ differ in that one is centrosymmetric at mercury while the other has a Ge—Hg—Ge angle of 178.68°, with a shortening of the contiguous Ge—Hg bond from 2.543 to 2.514 Å (*164*). In the absence of any meaningful intra- or intermolecular contacts, these phenomena must arise purely from packing effects. In contrast, the perfluoro analog, $[(C_6F_5)_3Ge]_2Hg$, which is also nearly linear at mercury, incorporates significantly shorter Ge—Hg bonds (2.483 Å) as a consequence of intramolecular coordination between one fluorine from each triorganogermyl group and mercury (*117*). No such bonds occur in $(C_6F_5)_3GeHgPt[P(C_6H_5)_3]_2Sn(C_6F_5)_3$, and the Ge—Hg bond lengthens again, to 2.534 Å (*116*).

The longest polymetallic chain known to date for any combination of metals is the nine-atom cluster $[(Ph_3GeCd)(Ph_3Ge)(\eta^5\text{-}C_5H_5)Ni]_2Cd$

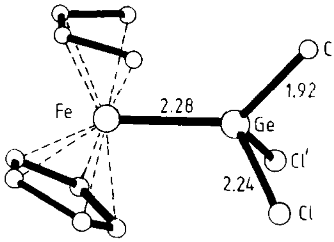


FIG. 17. The molecular structure of $(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_4H_6)FeGe(CH_3)Cl_2$. Bond lengths are in Å.

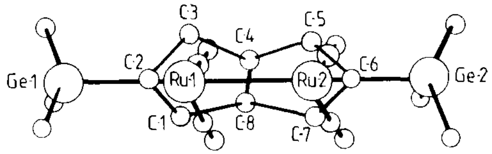


FIG. 18. The molecular configuration of $Ru_2[Ge(CH_3)_3]_2(CO)_4(C_8H_6)$, viewed perpendicular to the plane of the pentalene ligand.

(*163*). The molecule is made up of a zig-zag arrangement of germanium, cadmium, and nickel atoms, with localized linearity at cadmium and chain branching at nickel (Fig. 19). This compound also affords the only characterized examples of Ge—Ni (2.308 Å) and Ge—Cd (2.587 Å) bonds for an organogermanium compound.

Triangular clusters of three centers are formed when a diorganogermane bridges metal atoms which are themselves linked via a covalent bond. This is usually achieved by decarbonylation of a germanium bis(metal carbonyl). Structures have been reported in which the R_2Ge residue is the only bridging agent, e.g., in $\mu\text{-}\{[(C_6H_5)_4C_4H]C_6H_5Ge\}\text{-}Fe_2(CO)_8$ (*48*), $Cl[ClCH_2Si(CH_3)_2CH_2]GeFe_2(CO)_8$ (*35*), or when it is accompanied by a bridging carbonyl group as in $(CH_3)_2GeMn_2(CO)_9$ (*167*, Fig. 20). For the iron compounds, the Fe—Fe bond lengthens as bridging CO groups are replaced by the larger, germanium-based bridge (*1, 48*), a trend which would also serve to relieve angular strain within the acute Fe—Ge—Fe angle and repulsions between nonbonded, eclipsed, terminal carbonyls. In contrast, the Mn—Mn bond [2.854 Å (*167*)] in $(CH_3)_2GeMn_2(CO)_9$ is shorter than in the parent $Mn_2(CO)_{10}$ [2.923 Å (*52*)], an observation rationalized in a bonding model in which the Ge—Mn bonds are bent rather than along the line connecting the nuclei, the Mn—Mn bonding orbitals are delocalized and some bonding character is ascribed to the Mn—Mn antibonding molecular orbitals (*167*).

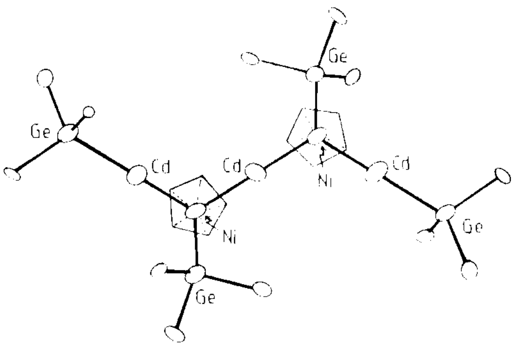


FIG. 19. The molecular structure of $\{(\eta^5\text{-}C_5H_5)[(C_6H_5)_3Ge][(C_6H_5)_3GeCd]Ni\}_2Cd$. Only the α-carbon atoms of each phenyl ring have been included.

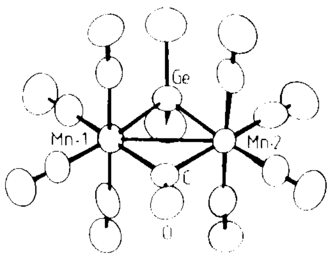


FIG. 20. The molecule of $(CH_3)_2GeMn_2(CO)_9$. Bond lengths (Å) are Mn-1—Mn-2, 2.854; Mn-1—Ge, 2.432; Mn-2-Ge, 2.477.

The Ge—Co bond exocyclic to the triangular $GeCo_2$ cluster in $C_6H_5Ge—CO_3(CO)_{11}$ is longer than both of the two endocyclic Ge—Co bonds by 0.64–0.81 Å (*13*).

Unique to this series of clusters based upon GeM_2 is the structure of the trimer, $[(CH_3)_2GeRu(CO)_3]_3$ (*93, 94*). Central to the molecular architecture is an Ru_3 ring, each side of which is bridged by the organogermyl group producing a six-membered heterocycle (Fig. 21), the first of its kind.

Replacement of the Fe—Fe bond and the bridging carbonyl group in $Fe_2(CO)_9$ with bridging RR′Ge moieties [R,R′ = C_2H_5 (*184*); R = Cl, R′ = $CH_2Si(CH_3)_2CH_2Cl$ (*35*)] yields square, GeFeGeFe clusters. For the haloorganogermyl compound (*35*), the nonbonding Fe ··· Fe distance (3.84 Å) is in excess of 1 Å greater than the Fe—Fe bond (2.814 Å) in the corresponding triangular $GeFe_2$ compound (*35*).

Derivatives of diiron enneacarbonyl, $Fe_2(CO)_9$, in which two or three of the bridging carbonyls are replaced by diorganogermanium linkages adopt a structure based upon a trigonal bipyramid. This is exemplified

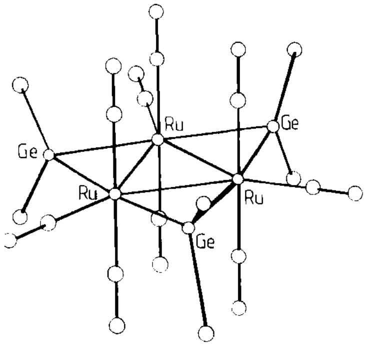


FIG. 21. The molecular structure of the $[(CH_3)_2GeRu(CO)_3]_3$ heterocycle. Bond lengths: Ru—Ru = 2.93 Å; Ru—Ge = 2.49 Å.

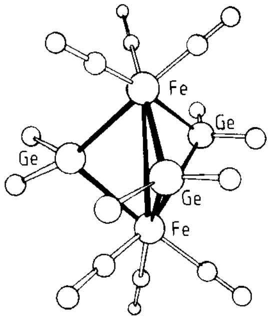


FIG. 22. The molecular structure of $[(CH_3)_2Ge]_3Fe_2(CO)_6$, showing the trigonal bipyramidal arrangement of heavy atoms.

by $[(CH_3)_2Ge]_3Fe_2(CO)_6$ (*33, 71*) in which the two iron atoms lie on a threefold axis (the axial sites on the trigonal bipyramid), with the three bridging germanium atoms girding this bond in the equatorial plane (Fig. 22). In $[(C_6H_5)_2Ge]_2Fe_2(CO)_7$, a bridging carbonyl replaces one of the R_2Ge moieties on an equatorial site, leaving a four-atom, Fe_2Ge_2 pyramid (*70*). Both of these compounds contain an Fe—Fe bond, which increases in length with increasing germanium substitution: 2.46 Å[3], $Fe_2(CO)_9$ (*142*) < 2.666 Å $[(C_6H_5)_2Ge]_2Fe_2(CO)_7$ (*70*) < 2.750 Å, $[(CH_3)_2Ge]_3Fe_2(CO)_6$ (*71*).

Isostructural with these iron compounds is the germanium–bismuth cluster $[(C_6F_5)_2Ge]_3Bi_2$ (*19;* Fig. 11) which can insert $Pt[P(C_6H_5)_3]_3$ to yield $[(C_6F_5)_2Ge]_3Bi_2Pt[P(C_6H_5)_3]_3$ (*19;* Fig. 12, see Section IV). The Ge—Pt bond length in this compound (2.466 Å) can be compared to a

[3] Cited as 2.523 Å in Ref. (*1*).

value of 2.433 Å in the square-planar *cis*-$[(OH)(C_6H_5)_2Ge](C_6H_5)[P(C_6H_5)_3]Pt$ (*78*).

VIII. Divalent Germanium Compounds

In keeping with the relative instability of the +2 oxidation state of germanium, few organometallic representatives of this class have been characterized (*119*). As with divalent tin (*49, 185*) stable R_2Ge compounds generally form when R is either cyclopentadiene (or one of its methylated derivatives) or a bulky ligand such as bis(trimethylsilyl)methyl. The structurally characterized $R_2Ge(II)$ compounds cover each of these ligand groups (see Addendum).

The donor properties of $\{[(CH_3)_3Si]_2CH\}_2Ge$ arising from the lone pair centered on germanium have been utilized in complex formation with a number of transition metal carbonyls. When this diorganogermanium(II) compound displaces CO from $Cr(CO)_6$, a donor–acceptor complex, $R_2GeCr(CO)_5$, results, in which the germanium exhibits the unusual coordination number of three (*119*). The orientation of the germanio group is such that the chromium atom and three carbonyl groups surrounding it are coplanar with the germanium and the methylene carbons to which it is bonded. The corresponding tin compound is isostructural (*46*), and a π interaction between chromium $3d$ orbitals and empty $5p$ or $5d$ orbitals on tin has been suggested.

IX. Addendum

Several organogermanium structures have recently been reported, and are herein included to up-date the literature surveyed.

Triphenylgermyl trifluoracetate crystallizes as discrete monomeric units, in which the geometry about the germanium is that of a distorted tetrahedron (*191*). The Ge—O bond length is 1.98 Å, with the second oxygen of the carboxylate group forming a weak, intramolecular coordinate bond (3.09 Å), distorting the geometry about the metalloid toward that of a trigonal bipyramid.

Interest in sterically hindered Group IVA ethers and thio-ethers continues, with the structure of $[(C_6H_5CH_2)_3Ge]_2S$ (*190*) being added to those already reported (Section V). The Ge—S—Ge moiety is nonlinear (106.6°) and the overall structure is similar to that of $[(C_6H_5)_3Ge]_2S$ (*113*).

Three cyclic organogermanium structures have appeared, embracing three-, four-, and six-membered ring systems. A triangular Ge_3

cluster is confirmed for the first time in $[(CH_3)_2C_6H_3]_6Ge_3$ (*195*), incorporating the longest known Ge—Ge bonds (2.537–2.543 Å). The Ge_3 triangle is essentially equilateral (∠Ge—Ge—Ge = 59.9, 60.1°) in contrast to the isoscelean arrangement in the trisilicon analog. The four-membered ring in $[(t\text{-}C_4H_9)_2GeS]_2$ appears planar (*197*), as is the six-atom heterocycle in $[(C_6H_5)_2GeO]_3$ (*196*). This latter, unique structure is suggested as a transition state model for twist-boat enantiomer racemization and C_6 chair–chair inversion processes.

Two additional structures utilizing organogermanes as ligands for transition-metal carbonyls have been elucidated, both involving a triorganogermyl cycloheptatriene π bonded to $Fe(CO)_3$. The triphenylgermyl compound, for which a full report has appeared (*194*), reveals an exo-disposition of iron carbonyl and organogermane with respect to the C_7H_7 ring, and η^4 bonding between ring and transition metal. A similar arrangement is also found in $(1\text{-}4\text{-}\eta\text{-}7\text{-}(CH_3)_3GeC_7H_7)Fe(CO)_3$ (*187*), although a full report of this structure has not yet been published.

Interest in five-coordinated germanium as exemplified by the germatranes (**6**) continues, with reports on two new structures, $CH_3Ge[(OCH_2CH_2)_2(CH_2)_3]N$ (*192*) and 1-germatranyl methylgermatrane (*193*), in addition to a complete description of the structure of $C_6H_5Ge[(OCH_2CH_2)_2(O_2CCH_2)]N$ (*186*) previously reported (*77*). All three species adopt the established trigonal bipyramidal structure (see Section IV), although in $CH_3Ge[(OCH_2CH_2)_2(CH_2)_3]N$ the intramolecular N: → Ge bond is unusually long (2.436 Å) reflecting a diminished Lewis acidity at germanium resulting from the absence of an electron-withdrawing oxygen in one arm of the chelating ligand (*192*).

A five-coordinated germanium at the center of a trigonal bipyramidal arrangement of ligands is also found in both $Cl_3GeCH_2CH_2COOH$ and $Cl_3GeCH_2CH_2CONH_2$ (*189*). In both cases, the expansion in coordination number at germanium from four to five arises from intramolecular C=O: → Ge bond formation, the oxygen occupying an apical position on the bipyramid trans to a chlorine (∠O—Ge—Cl = 166.0, 175.7°, respectively). In the amide the coordinate Ge—O bond is relatively short (2.166 Å) reflecting a stronger interaction than in the carboxylic acid in which the corresponding bond length is 3.228 Å. This results in the expected lengthening of the Ge—Cl bond trans to the oxygen from 2.134 Å in the acid to 2.253 Å in the amide.

Finally the structure of $[(CH_3)_5C_5]_2Ge(II)$ elucidated by electron diffraction (*74*) has been retracted (*188*). In the same report appears preliminary electron diffraction data on $(\eta\text{-}C_5H_4CH_3)_2Ge(II)$, an angular sandwich compound (angle between ring planes = 35°) with a mean Ge—C bond length of 2.53 Å, a structure significantly more in keeping with other metallocenes of the group (*5*, *99*) which are all angular sandwiches, with angles between the ring planes ranging from 36° for $[C_5(CH_3)_5]_2Sn$ (*99*) to ~55° for $(C_5H_5)_2Sn$ (*5*). An electron diffraction study of bis(pentamethylcyclopentadienyl) germanium yields a structure consistent with parallel, planar C_5 rings, although the data do not rule out structures in which the angle between the two rings is 10 or 20° (*74*). Even allowing for this uncertainty, the structure contrasts markedly with the corresponding lower Group IV analogs.

X. Conclusions

The primary goals of any review are twofold: to collate and précis existing data, while at the same time providing fertile ground in which ideas for further work can germinate. The body of the article, we hope, has provided the necessary collective data base, the yardstick against which new structures can be measured. In conclusion, we attempt to crystallize from that disparate collective, generalizations applicable to the whole of structural organogermanium chemistry and to suggest, albeit by inference, areas for further development. We enumerate these generalizations as follows:

1. The quality of the available data are generally of a reliable standard, particularly the more recent X-ray diffraction studies. Caution, however, must be exercised when evaluating much of the earlier gas phase work, in view of limitations in both contemporary instrumentation and experimental methods which usually require implicit assumptions about molecular geometry. Such data are generally best assessed in groups, and reliance given to systematic trends rather than absolute values.

2. Structures with coordination numbers of germanium at three, four, five and six have been determined, and adopt exclusively trigonal planar, tetrahedral, trigonal bipyramidal, and octahedral geometries about the metalloid, respectively. The square pyramidal geometry for five-coordinated germanium, recently characterized for the inorganic $[(C_6H_4O_2)_2GeCl]\,[(C_2H_5)_4N]^+$ (*150*), remains, as yet, unrealized for organogermanes, as do the examples of seven-coordinated pentagonal bipyramidal geometry, exemplified in organotin chemistry by, *inter alia*, $CH_3Sn(NO_3)_3$ (*34*) and $CH_3Sn[S_2CN(C_2H_5)_2]_3$ (*132*).

3. Angular deviations away from these regular geometries can usually be rationalized in terms of isovalent rehybridization theory (*16*).

4. Tetrahedral coordination predominates in the chemistry of the organogermanes, which in this respect compares more closely with silicon rather than with the chemistry of tin and lead. Enhanced coordination at the metalloid is predominantly a consequence of the steric demands of the ligands which surround it, e.g., five-coordinated organogermatranes (*12, 77, 87, 105*), or the six-coordinated diorganogermyl hemiporphyrazine (*92*). The Lewis acidity of tri- and diorganogermanium compounds appears generally too low to encourage interactions with Lewis bases, and it is to the relatively barren area of monoganogermanium chemistry that future workers may need to turn in order to evaluate more fully these higher coordinated states.

5. The lattice structures for organogermanes are predominantly molecular, with only isolated examples of associated lattices arising from intermolecular polymerization (*112, 152, 168*). It is, perhaps, surprising that so few examples exist in this area of chemistry in which molecular ordering signifies the onset of lattice association which is so common in organotin chemistry (*49, 185*).

6. There is no evidence to substantiate claims for $(p \rightarrow d)$-π bonding in these compounds, although shortening of the germanium–transition metal bond in almost all examples of such compounds suggests that overlap of *d*-orbitals leading to π bond formation may be energetically more favorable.

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NOTE ADDED IN PROOF: The structure of $(F_3C)_3GeMn(CO)_5$ has been reported and incorporates the shortest Ge—Mn bond (2.4132 Å) yet observed (*198*). The structure of 1,1-dimethylgermanocene in the gas phase has been described (*199*) as well as that of solid germanocene itself which is bent (angle between ring planes = 50.4°) with Ge—C bond lengths ranging from 2.3 to 2.7 Å (*200*). Alcoholysis with *t*-BuOH followed by treatment with $Ni(CO)_4$ gives $[(OC)_3NiGe(OBu\text{-}t)_2]_2$ whose structure is known (*201*).

The first anionic, pentacoordinated organogermane, triethylammonium bis(benzene-1,2-diolato)phenylgermanate $[(C_6H_4O_2)_2GeC_6H_5][(C_2H_5)_3NH]$ is 82% displaced from an ideal trigonal bipyramid toward a rectangular pyramid (*202*).