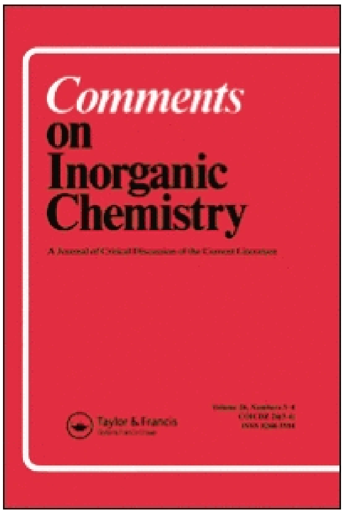

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Organometallic Compounds with Homonuclear and Heteronuclear Group IVb- Group IVb Bonds

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INTRODUCTION

The chemistry of carbon has three main features which form the basis of all organic chemistry, and which degrade the ensemble of all other elements in forming inorganic compounds to the small sister of organic chemistry. These features are catenation, multiple bonds, and functional groups.

Catenation enables the formation of long chains, branched chains, and rings made up of atoms of carbon only. Multiple bonds enable electrons to be shared by several carbon atoms and permit an easy change of coordination geometry at these atoms. The feature of functional groups is a selective attack at the group bearing carbon by a suitable reagent.

These three features are by no means unique to carbon. "The formation of stable, homoatomic linkages is an important property of most main-group elements."[1] The search for homoatomic multiple bonds other than those between carbon atoms has been very active in the last few years,[2–4] and there are abundant compounds bearing functional groups at elements other than carbon. Notwithstanding such efforts, one serious restriction remains. This is a lack of close connections between the three features mentioned above, and from this results a lack of reproducible procedures for preparing compounds with catenated inorganic elements. In fact, many such compounds are mentioned in the literature, but only a

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TABLE I

Homonuclear and heteronuclear bonds

M–M′	Si	Ge	Sn	Pb
Si	Si–Si	Si–Ge	Si–Sn	Si–Pb
Ge		Ge–Ge	Ge–Sn	Ge–Pb
Sn			Sn–Sn	Sn–Pb
Pb				Pb–Pb

fraction of them has been isolated in pure state and preparative amounts.

This Comment deals with compounds containing catenated elements of the fourth main group, which are stable and can be handled at room temperature. Table I lists, in the form of a matrix, the combinations of elements considered here: four homonuclear catenations and six heteronuclear catenations. These group IVb elements are able to catenate similar to the basic carbon–carbon skeletons of organic chemistry listed in Table II. There is, however, one major difference: in organic chemistry hydrogen is normally a stable ligand at carbon, and hydrocarbons C_nH_m of all kinds are very stable compounds. On the contrary, hydrogen bound to other group IVb elements forms functional groups, and stable com-

TABLE II

Generalized M–M′ skeletons (M, M′ = group IVb elements)

Analogues of Alkanes
ethane, propane, *n*-butane, iso-butane
n-pentane, neo-pentane, *n*-hexane

Analogues of Alkenes
ethylene

Analogues of Cycloalkanes
c-propane, c-butane, c-pentane
c-hexane

Analogues of Heterocyclic Compounds
1,4-dioxane, ethylene acetal
tetrahydrofurane
heterocyclic cages

pounds are only obtained if the hydrogen atoms are substituted by the organic groups shown in Table III. For this reason, all compounds considered in this Comment fall in the domain of organometallic chemistry. Figure 1 demonstrates one of the simplest examples.[5]

There seems to be a tendency for big and bulky groups to stabilize M–M′ skeletons, but except for this stereochemical effect no clear-cut difference exists between aliphatic and aromatic groups. The functional groups in the third column of Table III are the most useful ones in linking new M–M′ bonds.

SYNTHESIS

Compounds with Saturated M–M′ Bonds

Reaction (1) shows the main procedure for synthesizing all combinations given in Table I.

$$-\overset{|}{\underset{|}{\mathrm{M}}}\mathrm{Li} + \mathrm{Hal}\overset{|}{\underset{|}{\mathrm{M}}}'- \longrightarrow -\overset{|}{\underset{|}{\mathrm{M}}}-\overset{|}{\underset{|}{\mathrm{M}}}'- + \mathrm{LiHal} \qquad (1)$$

Two specific examples for obtaining an analogue of ethane[5] and an analogue of iso-butane are given in Eqs. (1a) and (1b).

$$\mathrm{Ph_3PbLi + ClGePh_3} \xrightarrow[-50^\circ\mathrm{C}]{\mathrm{THF}} \underset{\text{yield } 37\%}{\mathrm{Ph_3Pb{-}GePh_3 + LiCl}} \qquad (1a)$$

$$\mathrm{3\,Ph_3GeLi + Cl_3SiMe} \xrightarrow[-70^\circ\mathrm{C}]{\mathrm{DME}} \underset{\text{yield } 48\%}{\mathrm{MeSi(GePh_3)_3 + 3\,LiCl}} \qquad (1b)$$

TABLE III

Substituents at M–M′

Aliphatic	Aromatic	Functional
methyl	phenyl	Cl, Br, I
t-butyl	tolyl	trichloroacetyl
cyclo-hexyl	xylyl	R_2N
benzyl	mesityl	H
	naphthyl	Li, RMg
	anisyl	

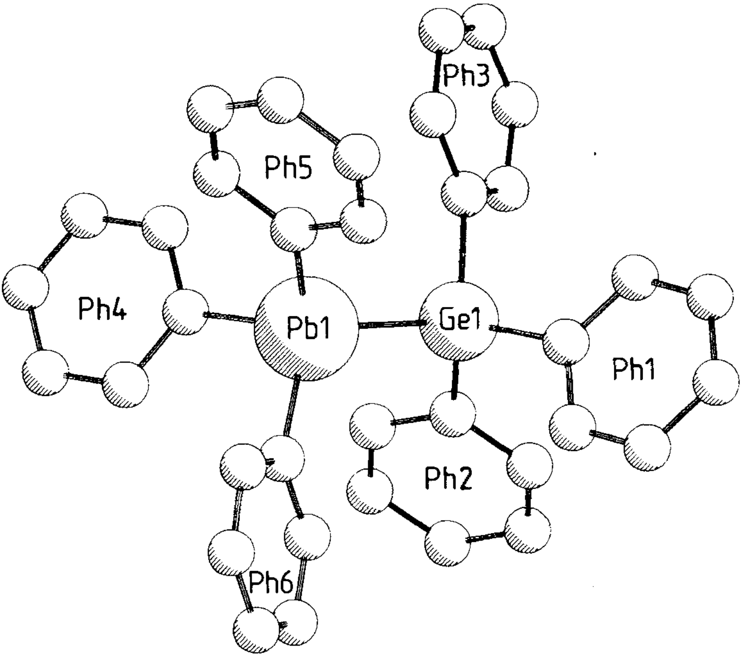

FIGURE 1 Analogue of ethane (Ref. 5).

In general, the products and yields from Eq. (1) type reactions are considerably dependent upon solvent and temperature. The main difficulty is to repress a nucleophilic attack of R_3M^- at newly formed M–M′ bonds. Reactions (2a) and (2b) show the formation of trigermanes.

$$Ph_3GeLi + R_2GeCl_2 \xrightarrow[-LiCl]{HMPT} Ph_3Ge{-}GeR_2Cl \tag{2a}$$

$$Ph_3GeLi + Ph_3Ge{-}GeR_2Cl \xrightarrow[-LiCl]{HMPT} Ph_3Ge{-}GeR_2{-}GePh_3 \tag{2b}$$

In competition with step (2b), Ph_3Ge^- can cleave the Ge–Ge bond formed in reaction (2a). This leads to a digermane on the one hand (chain stop reaction (2c)), and to a range of oligomers on the other hand (chain propagation reaction (2d)).[6]

$$\begin{tikzcd}[column sep=large]
\mathrm{Ph_3GeLi + Ph_3Ge{-}GeR_2Cl} \arrow[r] \arrow[d, "\begin{array}{l} +\ (n-1)\ \mathrm{R_2ClGeLi} \\ -\ n\ \mathrm{LiCl} \end{array}"] & \mathrm{Ge_2Ph_6 + R_2ClGeLi} \qquad \text{(2c)} \\
-(\mathrm{R_2Ge})_n- & \text{(2d)}
\end{tikzcd}$$

Reactions like (2c) are disadvantageous, whereas the chain propagating reaction (2d) is favorable. In any case, each step of a reaction like (1) must be followed up analytically by HPLC and structurally by mass spectroscopy. The best way to obtain smaller chains –M–M′– is the freezing out of newly formed products. For instance, the isolation of triplumbanes is only possible in this manner (1c).

$$\begin{tikzcd}
2\ (\text{c-Hex})_3\mathrm{PbLi} + \mathrm{Br_2Pb}(\text{c-Hex})_2 \arrow[r, "\mathrm{THF}", "-65\,^\circ\mathrm{C}"'] & {} \\
\mathrm{Pb_3}(\text{c-Hex})_8 + 2\ \mathrm{LiBr} \arrow[d, "-35\,^\circ\mathrm{C}"] & \\
\text{yield } 31\% & \text{(1c)}
\end{tikzcd}$$

Chain propagating reactions usually proceed better at medium temperatures. For instance, the normal Grignard reaction (1d) yields at room temperature the spectrum of products shown, which could be separated by a combination of flash chromatography and upscaled HPLC.[7]

$$n\ \mathrm{GeCl_4} + (2n+2)\ \mathrm{PhMgBr} + (n-1)\ \mathrm{Mg}$$

$$\xrightarrow{\mathrm{THF}} \mathrm{Ph(GePh_2)_{\mathit{n}}Ph} + (n+1)\ \mathrm{MgBr_2} + 2n\ \mathrm{MgCl_2}$$

$$\text{yields } n = 1,\ 53\%$$

$$n = 2,\ 17\%$$

$$n = 3,\ 11\%$$

$$n = 4,\ 18\% \qquad (1d)$$

Reaction (1) needs lithiated and halogenated starting materials. The first members are best prepared by cleavage of dinuclear compounds.[5,6] Mononuclear halogenated starting materials are obtained by distribution reactions. Polynuclear halogenated precursors are formed by selectively cleaving off two organic groups in perorgano compounds by trichloroacetic acid and subsequent reaction with HCl (e.g., Eq. (3)[8]).

$$\mathrm{Ge_2Ph_6} \xrightarrow[\mathrm{HAc}]{\text{toluene}} \mathrm{Ge_2Ph_4Ac_2} \xrightarrow[\mathrm{HCl}]{\text{acetone}} \mathrm{ClGePh_2{-}GePh_2Cl} \qquad (3)$$

Another good way for yielding α,ω-dihalogenated compounds is the method of germylene (|GeR_2) insertion into a Ge-H bond.[9] Equation (4) shows an example: good yields of digermane, trigermane and tetragermane are obtained in a one-pot-reaction with optimized ratio Ph_2GeHCl/NEt_3.

$$\mathrm{Ph_2GeHCl} \xrightarrow[\mathrm{NEt_3}]{\text{toluene}}$$

$$\mathrm{Cl{-}(Ph_2Ge)}_n\mathrm{{-}H} \xrightarrow[\mathrm{AIBN}]{\mathrm{CCl_4}} \mathrm{Cl{-}(Ph_2Ge)}_n\mathrm{{-}Cl}$$

$$\text{yields for } \mathrm{Ph_2GeHCl/NEt_3} = 1{:}2 \qquad n = 2,\ 23\%$$

$$n = 3,\ 21\%$$

$$n = 4,\ 36\% \qquad (4)$$

These α,ω-dihalo compounds are not only good precursors in reaction (1) but also for preparing the heterocyclic analogues listed in Table II.[10] A full range of all possible methods for obtaining saturated M–M′ compounds is reviewed, for instance for germanium, in Ref. 11. This review shows that hydrogen is an especially good functional group with increasing activity from silicon to lead.[12] Particular difficulties arise in attempts to link the two elements silicon and lead.[5] Only one successful example is known[13] (Eq. (5)).

$$2\,PbCl_2 + 2\,Mg(SiMe_3)_2 \xrightarrow[-78\,^{\circ}C]{Et_2O} Pb(SiMe_3)_4 + Pb + 2\,MgCl_2 \qquad (5)$$

Compounds with a M=M Bond

One of the most fascinating areas of chemistry over the last few years has been the synthesis of multiple bonds between elements other than carbon. Compounds with Si=Si or Ge=Ge have been prepared photochemically from a trisilane[2] (Eq. (6a)) or from a cyclotrigermane[14] (Eq. (6b)).

$$2\ Me_3Si{-}SiMes_2{-}SiMe_3 \xrightarrow{h\nu} Mes_2Si{=}SiMes_2 + 2\ Me_3Si{-}SiMe_3 \qquad (6a)$$

$$2(Ar_2Ge)_3 \xrightarrow{h\nu} Ar_2Ge{=}GeAr_2 \quad Ar = \text{2,6-dimethylphenyl},\ \text{2,6-diethylphenyl} \qquad (6b)$$

Another possible route starts from the germylene $GeCl_2{\cdot}dioxane$[15] (Eq. (7)).

$$2\ GeCl_2{\cdot}dioxane + 4\ RMgCl \xrightarrow[25\,^{\circ}C]{Et_2O} R_2Ge{=}GeR_2 + 4\ MgCl_2 + 2\ dioxane$$

$$R = CH(SiMe_3)_2 \qquad (7)$$

All these compounds are amazingly stable.

The first structural hint of compounds like those in Table II results usually from the mass spectrum. Yet for definite proof x-ray structure analysis is needed, and hence the growth of single crystals is the final step after successful synthesis.

Analogues of propane and butane have always expanded central bond angles (e.g., in Fig. 2 Pb–Pb–Pb 113.0°), and the conformation of n-butane like molecules is always *trans*.[16] Cyclopropane, -butane- and -hexane-like molecules exhibit rigid normal conformations, whereas analogues of cyclopentane are flexible.[17] Especially the three compounds $(Ph_2Si)_6$, $(Ph_2Ge)_6$ and $(Ph_2Sn)_6$, shown in Fig. 3, have nearly the same conformation.[18] Table IV lists the ranges of bond lengths found hitherto. The dependence upon substitution and branching is considerable.

Vibrational spectroscopy on these compounds is not very sensitive. Only the far infrared region below 400 wave numbers contains distinct spectra, and only the heavy atom lead enables ready assignments to be made (see Table V[5]). In all other cases the

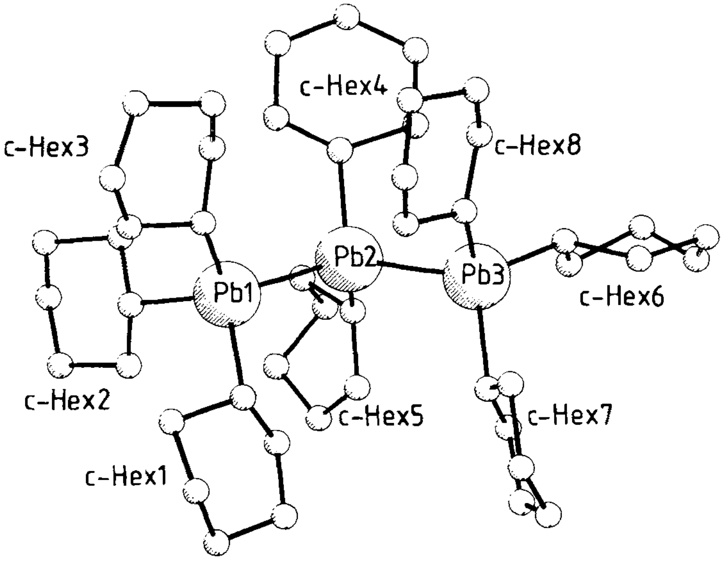

FIGURE 2 Analogue of propane.

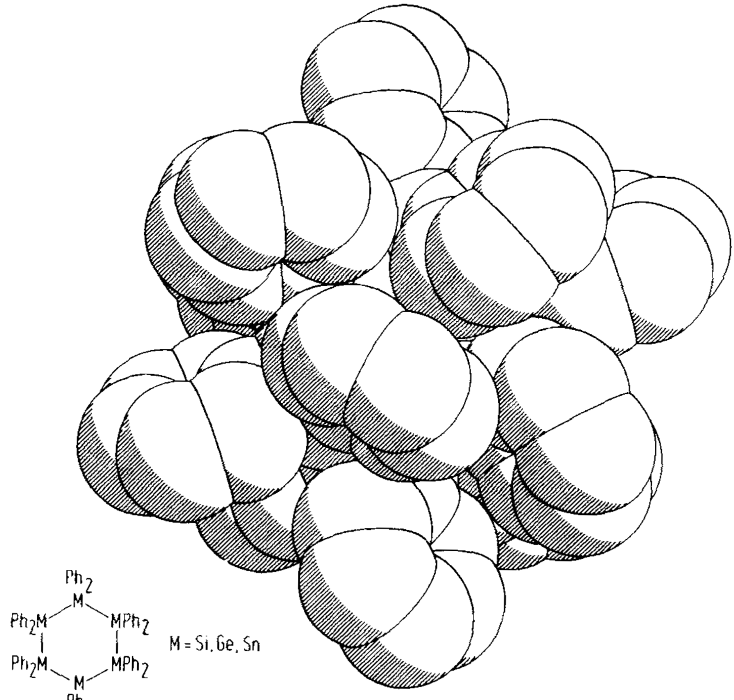

FIGURE 3 Analogues of cyclo-hexane (Ref. 18).

TABLE IV

Bond lengths (pm). Smaller values in cases of acetate-bridging (Ref. 8); larger values in cases of t-butyl substitution (Refs. 16 and 19)

M–M′	Si	Ge	Sn	Pb	M=M
Si	231–243	242–243	257–260	–	214–216
Ge		241–254	263–264	262–265	221–235
Sn			276–282	281–285	276
Pb				283–288	

skeleton vibrations couple strongly with vibrations in the organic groups. For this reason vibrational spectra are not more than fingerprints, unless a full normal coordinate analysis is possible in cases of small molecules. Fig. 4 shows one of the few examples accomplished.[20]

TABLE V

Vibrational data for analogues of ethane $Ph_3Pb-MPh_3$ (Ref. 5)

ν (Pb–Ge)	138 cm^{-1}
ν (Pb–Sn)	125 cm^{-1}
ν (Pb–Pb)	112 cm^{-1}

STRUCTURAL PROPERTIES IN SOLUTION

The fourth main group contains five spin-1/2 nuclei (^{13}C, ^{29}Si, $^{117,119}Sn$, ^{207}Pb), and for this reason NMR spectroscopy is a very powerful tool for most of the compounds considered. Both aspects, chemical shift δ and coupling constant *J*, give useful structural

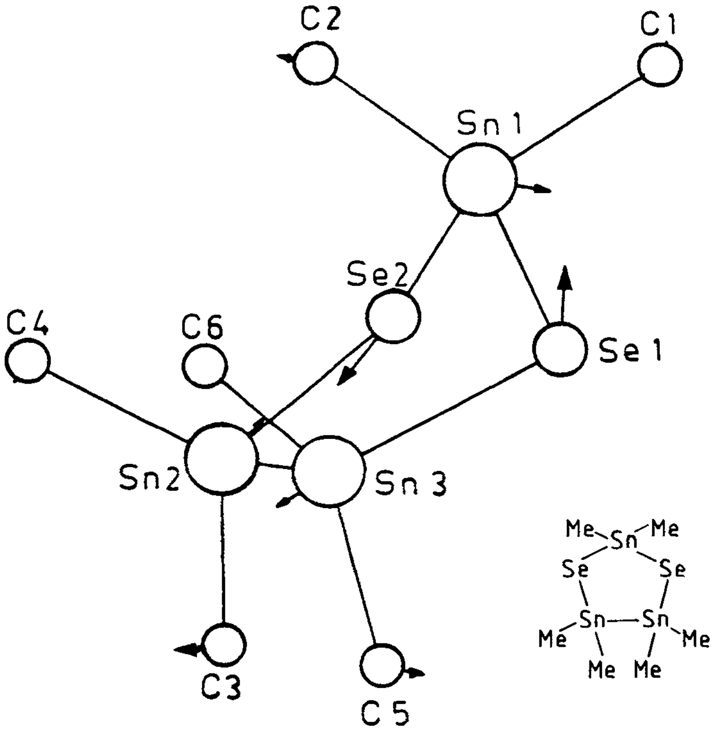

FIGURE 4 Analogue of ethylene acetal: ring vibration at 240 cm^{-1} with Cartesian displacements (Ref. 20).

information. Even the simple analogue of propane $Ph_3Sn-SntBu_2-SnPh_3$ shows a complicated but fully interpretable ^{119}Sn-NMR spectrum (Fig. 5; the signals not marked are couplings with ^{13}C).

THERMOANALYTICAL DATA

Up to now, none of the compounds of Table II have been of real interest for applied chemistry. Yet one aspect arises from thermoanalysis. Table VI lists enthalpies of transition and melting for some of the compounds.[6,17] The first are unusually high, the latter are low. These values and the behavior of the phases show that the compounds of Table VI transform into a plastically crystalline state[21] before melting. This state is comparable with the more

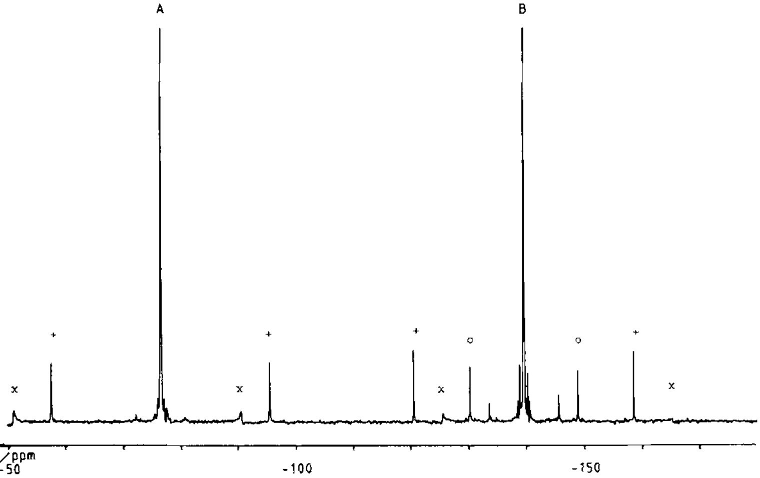

FIGURE 5 Analogue of propane $Ph_3Sn-SntBu_2-SnPh_3$: ^{119}Sn-NMR spectrum, isotopomers for skeleton $(^{X,Y,Z}Sn)_3$ marked (ina: inactive).

X - Y - Z					
119	ina	ina	7.4%	B	
ina	119	ina	3.7%	A	
119	117	ina	0.7%	BY	+
117	119	ina	0.7%	AX	+
119	ina	117	0.7%	BY	o
119	119	ina	0.8%	AB	x

TABLE VI

Enthalpies of transition and fusion

Compound	Transition T (°C)	 ΔH (kJ/mol)	Melting T (°C)	 ΔH (kJ/mol)
$(GeMe_2)_6$	71	16.5	237	3.6
$(SiMe_2)_6$	72	16.3	261	7.2
$(GePh_2)_5$	190	24.7	300[a]	
$Ph_3Ge(GePh_2)_2GePh_3$	227	54.9	350[a]	
$Ph_3Si(GePh_2)_2SiPh_3$	246	49.2	350[a]	
$Ph_3Ge-GePh_2-GePh_3$	248	45.3	293	3.0
$Ph_3Ge-SiPh_2-GePh_3$	252	38.9	293	2.2
$(GePh_2)_6$	346	32.5	450[a]	

[a] Decomposition.

familiar liquid crystals, and arises from the beginning of molecular torsions or rotations inside a still crystalline phase.[21] In accordance, all of the compounds of Table VI are nearly spherical (compare Fig. 6).

This property offers a possible application of the synthesized, stable compounds. Information accumulated inside the polymetal skeleton M_n can be adjusted to a special orientation above the transition point. Table VI includes a temperature scale in changing from one compound to the other.

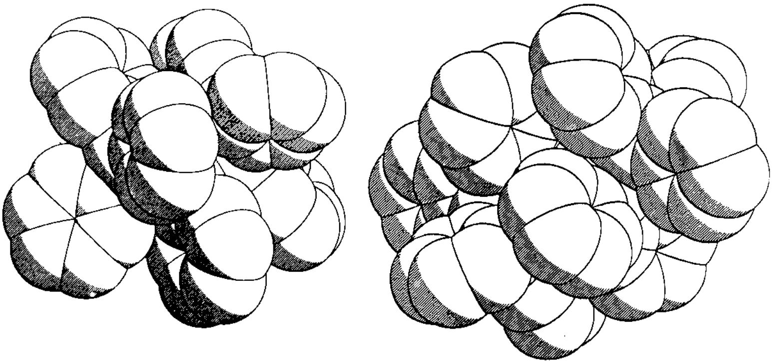

FIGURE 6 Analogues of propane Ge_3Ph_8 and n-butane Ge_4Ph_{10}: space filling models (Ref. 6).

CONCLUSION

Looking at the aspect of synthesis, the chemistry of polynuclear group IVb elements has only reached the mid-nineteenth century stage of organic chemistry. However, from a structural point of view, this chemistry is suitable for all modern tools of analysis. This area has stimulated work on improved syntheses in the past, and will certainly do so in the future.

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