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Multiply Bonded Germanium Species. Recent Developments

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I. Introduction

It was conventional wisdom for many years that compounds featuring double bonds between heavier main-group elements would not be stable because of weak $p\pi{-}p\pi$ bonding. Such a view is sometimes referred to as the "classical double-bond rule".[1] Due to many unsuccessful attempts to synthesize such species and to the assumptions of theoreticians,[1] this field lay dormant until the 1970s.

In the 1960s, transient molecules with double bonds between the heavier group 14 and 15 elements were detected spectroscopically or implicated from trapping experiments. The breakthrough in this field was the isolation in 1981 of the first stable compounds with $P{=}P$, $Si{=}C$, and $Si{=}Si$ double bonds. Researchers understood from these successful syntheses that oligomerization would be thwarted if sufficiently large ligands were utilized. Interestingly, despite the requisite steric blockades, kinetically stabilized compounds undergo a wide variety of chemical reactions at the double bond. Recent reviews have summarized this field.[2-9]

In the case of germanium, many studies have been conducted on transient and stable compounds of the type $>Ge{=}X$ (X = C<, Ge<, N–, P–, O, S, Se, transition metal). In 1984 the first stable multiply bonded germanium compound was synthesized in solution ($Ge{=}Ge$).[10]

The work on doubly bonded germanium derivatives reported before 1982 has been reviewed by Satgê[6] and will be briefly summarized in this paper. The reader should refer to Satgê's review for additional details.

The synthetic routes, physicochemical studies, and reactivity of $>Ge{=}X$ derivatives described in the present review have been particularly developed since 1982 and will be presented in the following order: $>Ge{=}C<$ (germenes), $>Ge{=}Ge<$ (digermenes), $>Ge{=}N-$ (germanimines), $>Ge{=}P-$ (germaphosphenes), $>Ge{=}O$ and $>Ge{=}S(Se)$ (germanones and germanethi(selen)ones), and $>Ge{=}Mn$.

II. $Ge{=}C$ Species: Germenes

(1) Transient Germenes

Germenes 1, species containing a $p\pi{-}p\pi$ double bond between germanium and carbon, are among the most intensively investigated topics in germanium chemistry. To briefly summarize the different routes to transient germenes, it is noted that the three most important are (1) the thermal decomposition of bicycles 2[11] (Diels–Alder adducts of germacyclohexadienes with alkynes), (2) the photolysis or pyrolysis of (trimethylgermyl)diazomethanes 3[12-14] with methyl migration from germanium to carbon, and (3) a direct interaction between a germylene 4 and a carbene generated in situ.[15] Other routes have also been described, such as the thermolysis of $PhOGe(R_2)CH{=}CH_2$,[16] the reaction between cyclopentadienylchlorodiethylgermane and a phosphorus ylide,[17] or the reaction between [bis(trimethylsilyl)bromomethyl]lithium and dimethyldichlorogermane.[18] However, in the last case, another process not involving a germene intermediate is considered more likely (Scheme 1).

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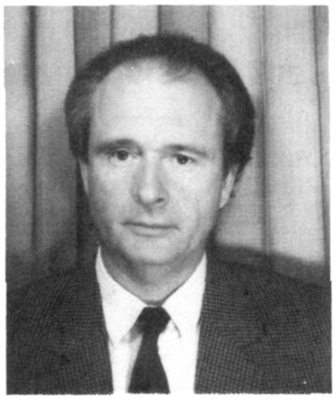


Jacques Barrau was born in 1942 in Toulouse, France. He received his "3rd cycle" degree (Ph.D.) in 1969 and his Doctorat d'Etat (Habilitation) in organic chemistry in 1973 from the University of Toulouse for research undertaken with Professor J. Satgé on heterocycles and divalent M_{14} species (M_{14} = Ge, Sn). He is currently Associate Professor at the University of Toulouse. In 1987–1988 he was Visiting Professor at The University of Texas at Austin in the laboratory of Professor J. Michl, working on the matrix isolation of reactive germanium-containing intermediates. His main research interests include the chemistry of intermediates containing divalent and $p\pi$–$p\pi$-bonded group 14 metals (with emphasis on germanium species) and the chemistry of polynuclear heterocycles having C–M_T–M_{14} linkages.

Jean Escudié was born in 1946 in Decazeville, France. He received his "3rd cycle" degree (Ph.D.) in 1970 and his Doctorat d'Etat (Habilitation) in 1978 from Paul Sabatier University in Toulouse, working with Professor J. Satgé on germanium chemistry. In 1979 he joined Dietmar Seyferth's group for a 1-year period as a postdoctoral fellow at the Massachusetts Institute of Technology, where he worked on silacyclopropanes and disilacyclobutanes. Since leaving Professor Seyferth's group he has been studying low-coordinated species of main-group elements such as M═M': (M, M' = B, C, Si, Ge, Sn, P, As). He is currently Directeur de Recherche at the C.N.R.S. in Toulouse.

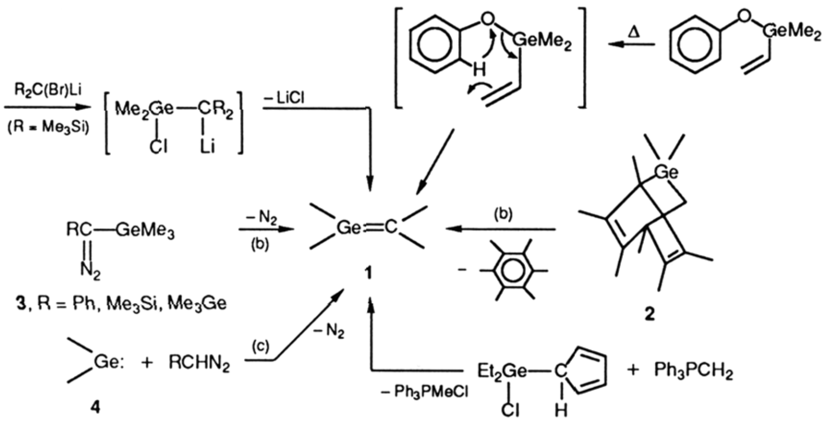
Jacques Satgé was born in Gaillac, France, in 1929. He received his Doctorat d'Etat (Habilitation) in chemistry in 1961 from the University of Toulouse. He became full Professor in 1971 in the organic chemistry chair of Paul Sabatier University, Toulouse (1979). Professor Satgé's research interests include the organometallic chemistry of group 14 elements (germanium, silicon, tin, lead), group 15 elements (nitrogen, phosphorus, arsenic), and also sulfur, boron, and transition-metal complexes, with emphasis on the synthesis, reactivity, physical chemistry, and application of organometallic species in low coordination states. Professor J. Satgé is Director of C.N.R.S. associate laboratory UA 477, is a laureate of the C.N.R.S., the French Chemical Society, and the French Academy of Sciences, and is a member of the National Comity of Universities.

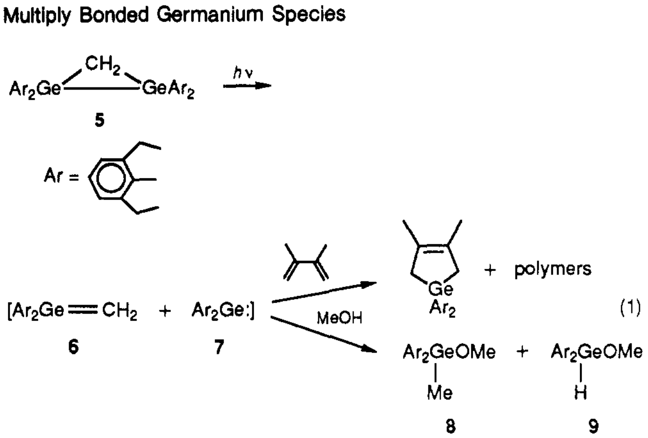
These transient germenes were trapped in situ with alcohols, dienes, aldehydes, nitrones, and nitrosobenzene.[15] In the absence of trapping reagents, the formation of dimers was observed.

A transient germabenzene was postulated by Märkl[19] as an intermediate formed during the dehydrobromination of the corresponding germacyclohexa-2,4-diene, and its dimerization or Diels–Alder product has been characterized. These various routes, which allowed the first evidence of the formation of transient germenes, and some other new methods have been developed since 1982 and are described below.

The formation of germene **6**[20] was demonstrated by in situ trapping with methanol in the photolysis of the digermirane **5** (eq 1). The formation of the products **8** and **9** in good yields clearly indicates that digermirane **5** is fragmented into the corresponding germene **6** and germylene **7**. While germylene **7** reacts efficiently with butadiene and methanol, germene **6** did not react with the butadiene and undergoes polymerization. Note,

SCHEME 1

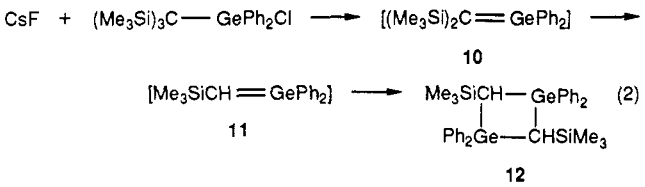




(1)

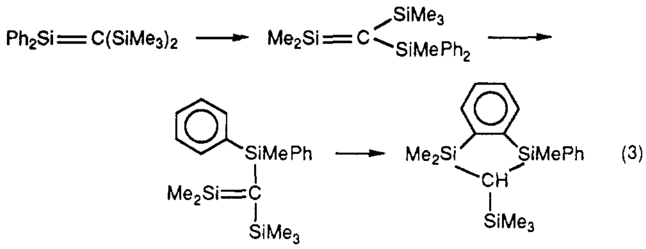
however, that germenes obtained by routes other than irradiation give good yields of cycloadducts with dienes (see below).

Generation of a transient germene **10**[21] was postulated in the reaction of $(\mathrm{Me_3Si})_3\mathrm{CGePh_2Cl}$ with cesium fluoride. Surprisingly, this reaction provides, in good yield, **12**, which was characterized by X-ray analysis. It is assumed that the precursor of **12** is the germene **10**, which because of steric hindrance, cannot undergo cyclodimerization and loses a $\mathrm{Me_3Si}$ group to give a second transient germene **11** followed by cyclodimerization to give **12** (eq 2).



$$\mathrm{CsF} + (\mathrm{Me_3Si})_3\mathrm{C{-}GePh_2Cl} \longrightarrow \underset{\mathbf{10}}{[(\mathrm{Me_3Si})_2\mathrm{C{=}GePh_2}]} \longrightarrow \underset{\mathbf{11}}{[\mathrm{Me_3SiCH{=}GePh_2}]} \longrightarrow \underset{\mathbf{12}}{\begin{matrix}\mathrm{Me_3SiCH{-}GePh_2}\\ |\qquad\quad |\\ \mathrm{Ph_2Ge{-}CHSiMe_3}\end{matrix}} \quad (2)$$

The problem of how the $\mathrm{Me_3Si}$ group undergoes exchange with a proton remains unresolved. In contrast, the transient silicon analogue of **10**, $(\mathrm{Me_3Si})_2\mathrm{C{=}SiPh_2}$, undergoes a 1,3-migration of a methyl group, followed by C–H insertion at the ortho positions of the phenyl substituent (eq 3).

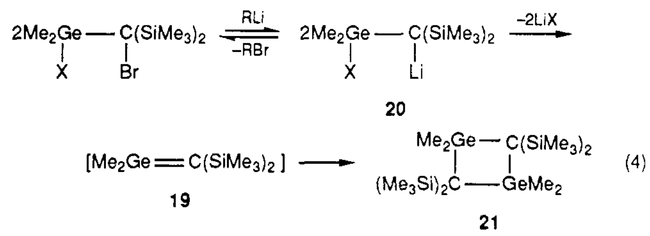


(3)

The formation of the transient germene $\mathrm{Me_2Ge{=}CH_2}$ (**13**)[23] has been observed in attempts to synthesize the four-membered-ring oxagermetane $\mathrm{Me_2Ge{-}CH_2{-}O{-}CH_2}$ (Scheme 2). Classical routes to oxetane, when applied to the dihalogenated germane **14**, led to germoxane **15** instead of the expected cyclic product. An elimination reaction, with formation of formaldehyde and germene **13**, followed by a [2 + 2] cycloaddition leading to germaoxetane **16** and a retro [2 + 2] reaction are postulated in order to account for this result. Evidence of the transient formation of **13** comes from its trapping with water or ethanol to give **17** and **18** (Scheme 2).

The formation of transient digermene $\mathrm{Et_2Ge{=}GeEt_2}$ and germene $\mathrm{Et_2Ge{=}CHPh}$ has been invoked in the pyrolysis of a digerma-1,2-cyclohexene in the presence of benzaldehyde (see section III.1).

Recently, the transient germene $\mathrm{Me_2Ge{=}C(SiMe_3)_2}$ (**19**)[24] has been obtained by Wiberg following thermal elimination of LiX (between −110 and +100 °C, depending on X) from **20**. In the absence of suitable trapping reagents the dimer **21** is obtained (eq 4). Note

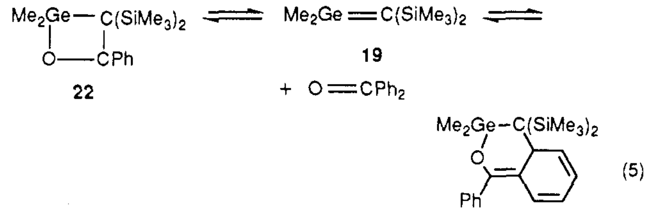


(4)

X = F, Br, OMe, OPh, $\mathrm{OC_6F_5}$, $\mathrm{OC_6H_3Cl_2}$, SPh, $\mathrm{Ph_2PO_4}$, $\mathrm{Ph_2PO_2}$

that the chemical behaviors of **10** and **19** are completely different, since **19** easily dimerizes, whereas **10**, substituted on germanium by two phenyl groups, which are slightly bulkier than the methyl group (as in the case of **19**), cannot dimerize and instead loses a trimethylsilyl group.[21] Germene **19** has been thoroughly characterized by its chemical reactivity: both by insertion into the O–H bond of alcohols[25a] and by ene reactions.[24,25a] Various cycloadditions[24,25] have also been observed: [2 + 2] cycloadditions are obtained with the C=C bond of $\mathrm{CH_2{=}CHOMe}$[25a] and the C=O bond of ketones,[25a] [2 + 3] cycloadducts with azides[25] and $\mathrm{N_2O}$,[25] and [2 + 4] cycloadducts with dienes. However, in the case of dimethylbutadiene, a competition occurs between ene reaction and cycloaddition[24,25a] (Scheme 3). The five-membered-ring derivatives **23** obtained by cycloaddition of azides are good precursors of germanimines (>Ge=N–). Most of the reactions of germenes are regiospecific, the first step probably being the nucleophilic attack on germanium[25a] (Scheme 3).

In the case of benzophenone, both [2 + 2] and [2 + 4] cycloaddition occur, but [2 + 2] cycloaddition is predominant (83%). The adduct **22** can be considered as a "store" for germene **19** since it decomposes very easily to the germene and benzophenone by thermal cycloreversion (eq 5).[25a]

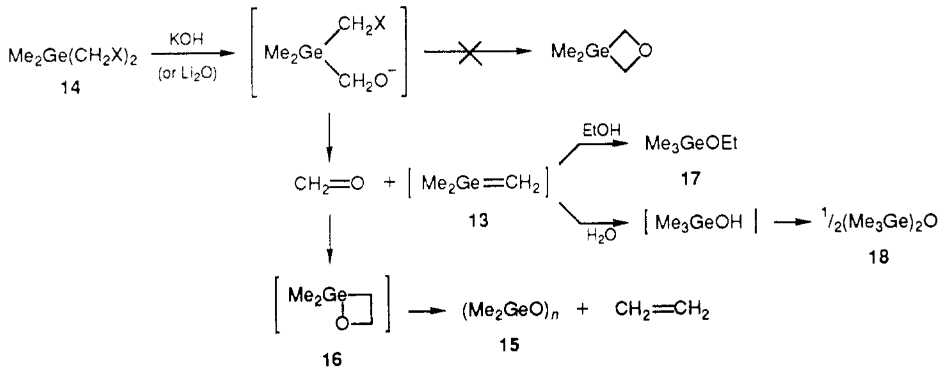


(5)

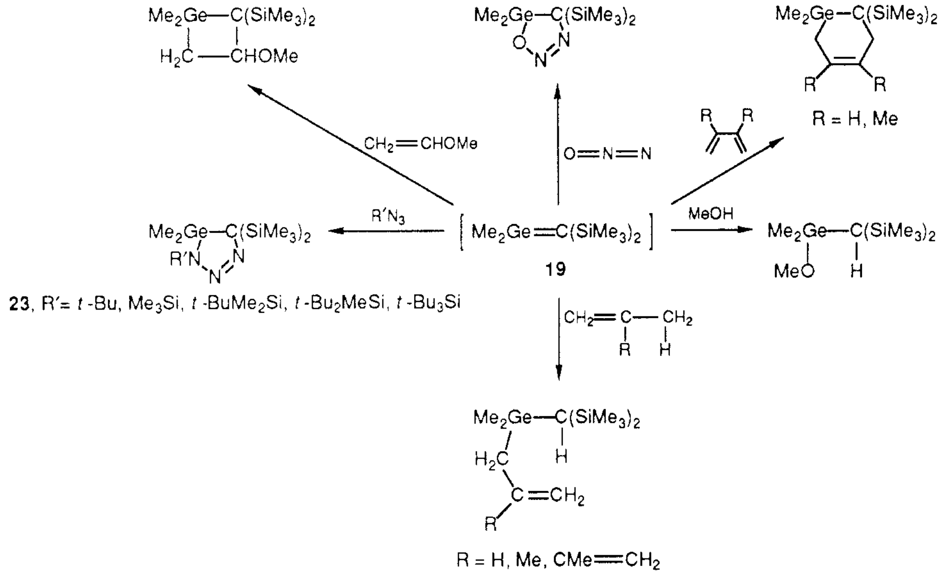
By comparison with the silaethene $\mathrm{Me_2Si{=}C(SiMe_3)_2}$, **19** is less Lewis acidic and its double bond is less polar,[25a] as predicted by calculations.[26]

Thermolysis, pyrolysis, and photolysis of various heterocycles such as thiagermetane $\mathrm{Me_2Ge{-}CH_2{-}S{-}CH_2}$,[27,28] dithiagermolane $\mathrm{Me_2Ge{-}CH_2{-}S{-}S{-}CH_2}$,[28] 2,4-digermetane $\mathrm{Me_2Ge{-}CH_2{-}GeMe_2{-}O}$,[29] 2,4-digermathietane $\mathrm{Me_2Ge{-}CH_2{-}GeMe_2{-}S}$,[30,31] and thiagermetane dioxide $\mathrm{Me_2Ge{-}CH_2{-}SO_2{-}CH_2}$[28] lead to both germenes $\mathrm{Me_2Ge{=}CH_2}$ and germanones $\mathrm{Me_2Ge{=}O}$, germanethiones $\mathrm{Me_2Ge{=}S}$, or germanesulfenes $\mathrm{Me_2Ge{=}SO_2}$. Germenes and germanethiones have also been characterized[32,33] in the reaction of dimethylgermylene

SCHEME 2

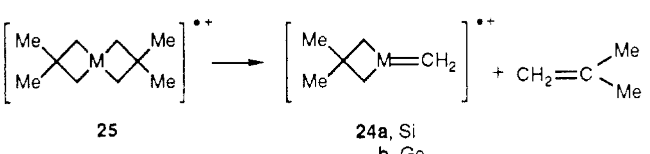


SCHEME 3



(Me_2Ge) (generated from germanorbornadiene) and adamantanethione. All these reactions leading to both germenes and germanethiones are described in section VI.

Evidence for germenes and germabenzenes has been obtained by physicochemical methods. The 1-methylenemetallacyclobutenes **24**[34] for example are observed from precursors **25** (eq 6). In the mass spectra



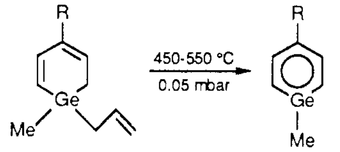
25

24a, Si
b, Ge

(6)

of these spiro compounds of silicon and germanium, a relatively abundant fragment ion $[M - C_4H_8]^+$ appears. In view of the well-established cleavage of silacyclobutanes into silenes and ethylene[35] under electron impact conditions, an analogous cleavage can be suggested in this case leading to silenes and germenes **24** (eq 6). It should be pointed out that, in contrast to observation on the monocyclic group 14 metallacyclobutanes, the $[M - C_4H_8]^+$ ions do not form the base peak; further fragmentation is evident, in particular the loss of an additional methyl group.

Germenes have also been detected in the mass spectra of four-membered-ring germaoxetanes obtained by addition of aldehydes or ketones to a stable germene (see section II.2.c). Three 1,4-dialkylgermabenzenes **26**[36] generated from the corresponding allylcyclohexadienes **27** by gas-phase pyrolysis have been spectroscopically detected in the gas phase by VTPES (variable-temperature photoelectron spectroscopy) experiments (eq 7). Various silabenzenes were detected earlier in a similar manner.[36]



(7)

27 **26**

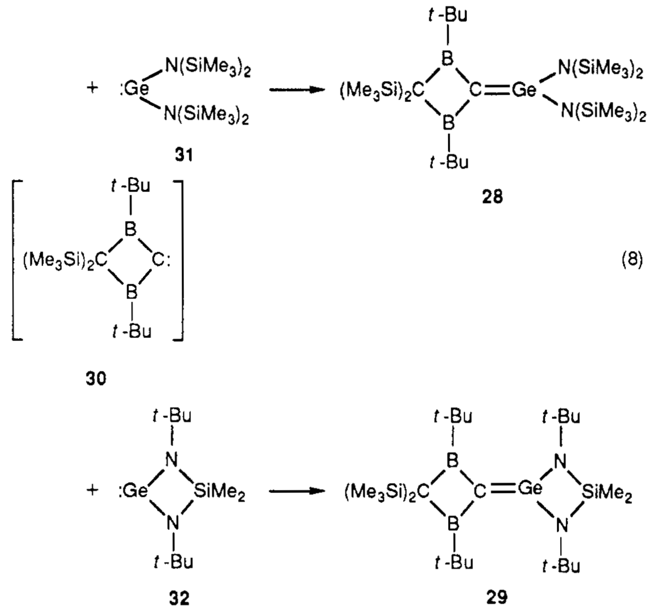
R = Et, *i*-Pr, *t*-Bu

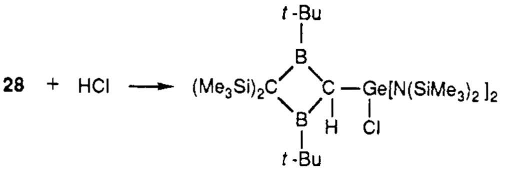
(2) Stable Germenes

(a) Synthesis

The use of steric and electronic stabilization allowed the isolation of three stable germenes by Berndt[37,38] and by some of us[39,40] in 1987. The Berndt compounds **28** and **29**[37,38] were synthesized by the reaction between the electrophilic cryptocarbene **30** and the stable germylenes **31**[41] and **32**[42] at room temperature (eq 8).

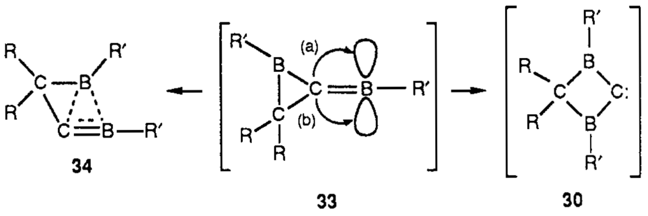
The germene structure of **28** and **29** has been proved by NMR (see Figure 1) by addition of HCl onto the germanium–carbon double bond (eq 9) and in the case of **28** by X-ray crystallography.





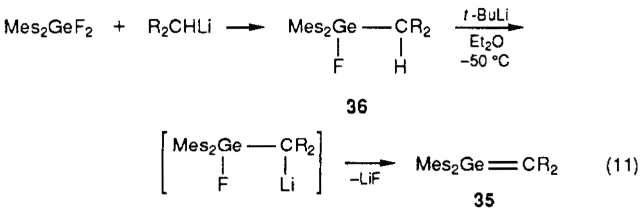
(9)

The starting cryptocarbene **30** is the nonclassical boranediylborirane **33**[43] (eq 10): interaction of the empty p orbital at the dicoordinated boron with the adjacent B–C σ bond (a) of the three-membered ring yields **34**; stronger interaction with the C–C σ bond (b) can lead to carbene **30**, which has recently been calculated to be only 10 kcal/mol higher in energy than **34** for model compounds with R = SiH_3 and R′ = CH_3.[44] It was shown experimentally that **33** behaves as a carbene in the reactions with bis(trimethylsilyl)ethyne, triphenylphosphine, and triphenylarsine.[45]

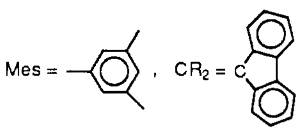


R = Me_3Si, R′ = t-Bu (10)

In our laboratories the stable germene **35**[39,40] was prepared by dehydrofluorination of the corresponding fluorenyl germane **36** at low temperature (eq 11).



$$Mes_2GeF_2 + R_2CHLi \longrightarrow Mes_2GeF{-}CHR_2 \xrightarrow[\substack{Et_2O\\-50\ °C}]{t\text{-BuLi}} [Mes_2GeF{-}CLiR_2] \xrightarrow[-LiF]{} Mes_2Ge{=}CR_2 \quad (11)$$



Germene **35** is very thermally stable but highly air sensitive. As other doubly bonded main-group compounds, it is thermochromic: it is yellow at −100 °C, orange at room temperature, and orange-red at +80 °C. It forms stable B→>Ge=C< adducts with Lewis bases such as ethers or amines; this type of complexation has also been observed with silenes (>Si=C<)[46,47] and silanimines (>Si=N–)[48–50] but never in symmetric molecules M=M (M = Si, Ge, Sn, P) or in metallaphosphenes M′=P (M′ = Si, Ge, Sn) where the group 14 metal is bound to phosphorus, a less negative atom than carbon or nitrogen.[51,52] The complexation reactions of **35** are easily explained by the electrophilic character of germanium and the polarity of the Ge=C bond (the dipole moment of **35** is estimated to be 4 D;[40] see below).

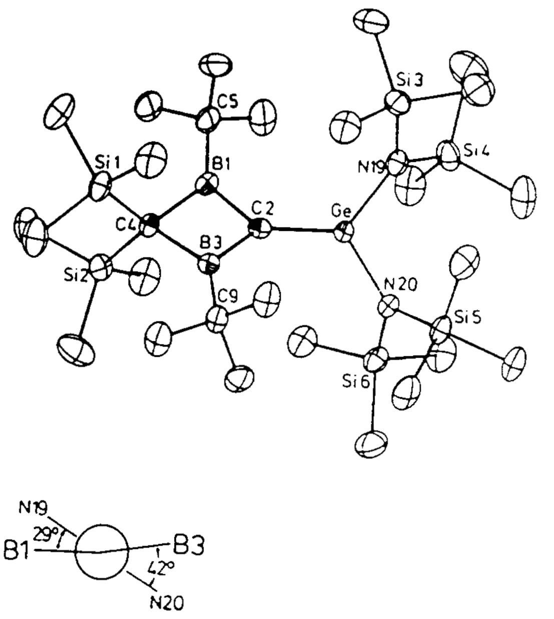


Figure 1. ORTEP view of **28** (reprinted from *Angew. Chem., Int. Ed. Engl.* 1987, *26*, 799; copyright 1987 VCH Verlagsgesellschaft mbH).

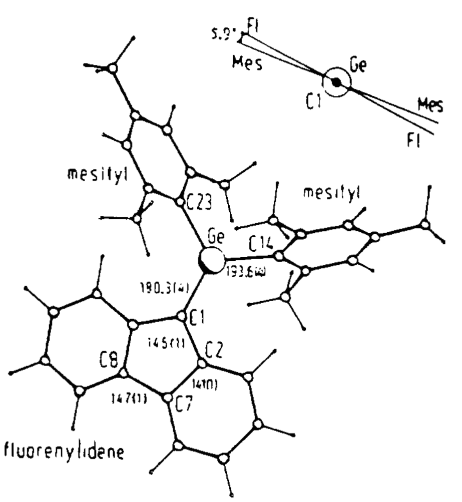


Figure 2. ORTEP view of **35** (reprinted from *Angew. Chem., Int. Ed. Engl.* 1988, *27*, 828; copyright 1988 VCH Verlagsgesellschaft mbH).

(b) Physicochemical and Theoretical Studies

The ^{13}C NMR shows for **28** and **29** the expected low-field signals for the carbon doubly bonded to germanium (respectively 115 and 93 ppm), whereas the ^{11}B NMR shows a shielded boron atom, indicating that

TABLE 1. Calculated d(Ge=C) and ν(Ge=C) for $H_2Ge=CH_2$

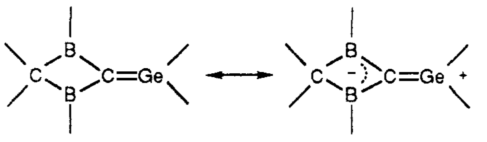
	ab initio using pseudopotentials[a]		
	SCF	CI	MNDO[b]
d(Ge=C), Å	1.779	1.812	1.717
ν(Ge=C), cm^{-1}	906	847	854

[a] Reference 27. [b] Reference 55.

TABLE 2. Calculated and Experimental Physicochemical Values for 35 and 37

property	germane 37	germene 35
ionization energy, eV	8.50	7.26
bond order		
Ge=C	0.77	1.50
Ge—C(Mes)	0.79	0.86
charge distribution		
Ge	+1.66	+1.53
C(fluorenyl)	−0.34	−0.62
C(Mes)	−0.42	−0.43
d(Ge—C), Å	2.01	
d(Ge=C), Å		
exptl		1.80
calcd (MNDO)		1.77
ν(Ge=C), cm^{-1}		
exptl		988
calcd (MNDO)		1018

there is a relatively large amount of negative π charge on these atoms and an ylidic character to the molecule (eq 12).



(12)

28A, 29A **28B, 29B**

An X-ray structure analysis of **28** (Figure 1) confirmed the significance of the ylide resonance form B as shown by short distances C(Ge)–B and an average twist angle at the Ge=C bond of 36°.[37,38] The germanium–carbon double bond (1.827 Å) is about 8.4% shorter than the Ge–C bond in $GeMe_4$ (1.98 Å). Similar contractions are observed for silenes.[3,4] The X-ray structures of both $Mes_2Ge=CR_2$ (**35**) (Figure 2) and $Mes_2Ge(H)C(H)R_2$ (**37**) have been obtained[40] and allow a good comparison between Ge–C single and double bonds. The Ge=C double bond (1.80 Å) is about 10.5% shorter than the corresponding Ge=C single bond in **37** (2.01 Å) and constitutes a very large shortening. The germanium atom is planar, and the twisting around the Ge–C bond is only 6° (compared to 36° in **28**).[37,38] This finding, namely that 16 atoms lie nearly in the same plane despite high steric strain, supports the postulate of a stabilization of **35** by electronic interaction between the Ge=C double bond and the fluorenylidene moiety. Similar stabilizations of a P=C[53] and of a B=C[54] double bond by the fluorenylidene system are known; for P=C, interactions with the fluorenylidene π electrons have been proposed.

The results of the X-ray structure of **35** are in good agreement with ab initio[26] or MNDO[55] calculations which predicted a planar structure for $H_2Ge=CH_2$. On the other hand, $H_2Ge=CF_2$ is predicted to be nonplanar by calculations.[56] The germanium–carbon double-bond length in $H_2Ge=CH_2$ has been predicted by various methods to be between 1.71 and 1.81 Å (see Table 1).

TABLE 3. π-Bond Energy of $Me_2M=CH_2$ (M = C, Si, Ge, Sn) (kcal/mol)

method	$H_2C=CH_2$	$H_2Si=CH_2$	$H_2Ge=CH_2$	$H_2Sn=CH_2$
a[a]	64–66	35–36	31	19
b[b]	67–68	35	31	19

[a] Method a: direct energy differences between planar (π bonded) and perpendicular (biradical) structures. [b] Method b: from disproportionation energies.

TABLE 4. π-Bond Strength of $Me_2M=CH_2$ (M = Si, Ge, Sn, Pb) (kcal/mol)

$Me_2Si=CH_2$	$Me_2Ge=CH_2$	$Me_2Sn=CH_2$	$Me_2Pb=CH_2$
38	43	45	30

Semiempirical calculations have also been made on **35**. The MNDO optimization of the geometrical parameters gives a Ge=C bond length of 1.77 Å,[57] in relatively good agreement with the X-ray analysis[40] (see Table 2).

The Raman spectrum of crystalline **35** shows an emission at 988 cm^{-1}, which is attributed to the Ge=C valence vibration.[40] This assignment was corroborated by ab initio calculations using pseudopotentials[26] (see Table 2). A comparison has been made by MNDO calculations between germene **35** and germane **37**. The results for ionization energy,[57] bond order,[57] charge distribution,[57] and bond lengths[40] are listed in Table 2.

The charge distributions for $H_2Ge=CH_2$ and $H_2Si=CH_2$ have been calculated by using double ζ + d (Ge and C) basis sets; the charge difference in silenes is predicted to be greater than in germenes[26] (eq 13), in agreement with the Allred–Rochow electronegativity scale[51,52] and with their chemical reactivity.

(13)

Other calculations on charge distribution have been performed on germenes, particularly on the fluorinated germenes $H_2Ge=CF_2$, $F_2Ge=CH_2$, and $F_2Ge=CF_2$. They were predicted to have an unusual double bond having a relatively weak σ bond and much stronger π bond, which is polarized $Ge^{\delta+}–C^{\delta-}$.[58]

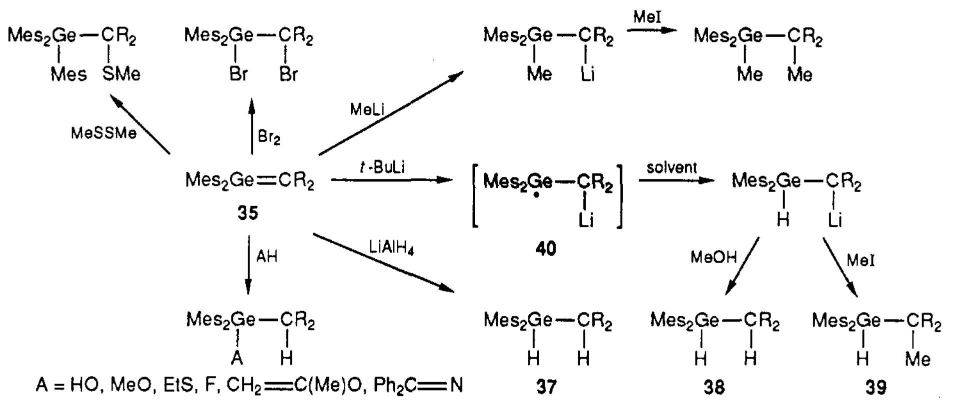
The π-bond energies of the M=C bonds in $H_2M=CH_2$ have been determined by various methods[59] (see Table 3). Pietro and Hehre[60] have estimated the π-bond strength of $Me_2M=CH_2$ (M = Si, Ge, Sn, Pb) on the basis of gas-phase deprotonation thresholds for group 14 trimethylmetalla cations Me_3M^+ (M = Si, Ge, Sn, Pb) (Table 4). These authors have noted, however, that the values for the germanium and tin systems appear to be out of line with the π-bond strengths in silicon compounds due to experimental thermochemical data of uncertain quality.

Calculations have been performed comparing the relative stabilities of germene ($H_2Ge=CH_2$) and methylgermylene (HGeMe). All the calculations[26,61,62] show that the germene is less stable than the germylene by about 15,[26] 17.6,[61] 23,[62] 24.2,[61] and 24.8[61] kcal/mol, depending on the calculation method and on the basis sets considered.

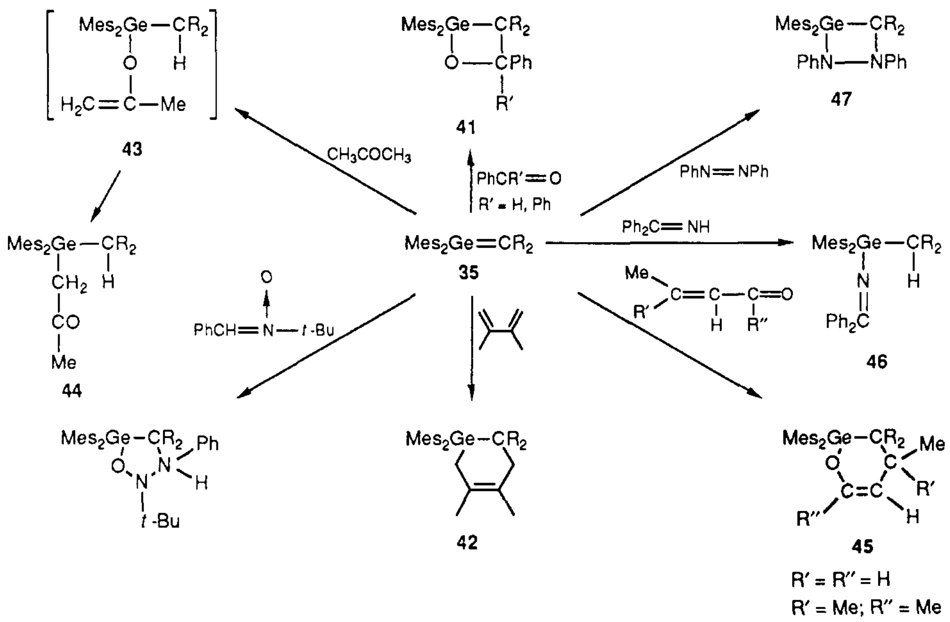
(c) Chemical Reactivity of 35

Germene **35** is highly reactive toward various electrophiles and nucleophiles (Scheme 4). For example,

SCHEME 4

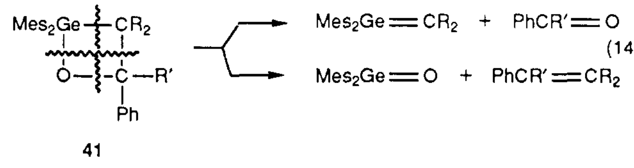


SCHEME 5



protic reagents,[39,63] halogens,[63] and lithio compounds[63] add very easily onto the double bond. Reduction of **35** can be effected by $LiAlH_4$.[39] With *tert*-butyllithium, derivatives **38** and **39** are obtained after quenching with methanol and methyl iodide; these reactions probably involve radical intermediate **40**. An addition of dimethyl disulfide onto the double bond has also been observed[39] (Scheme 4).

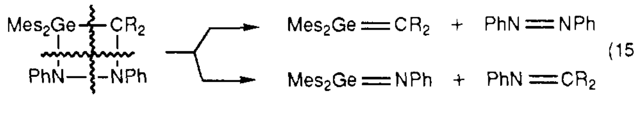
Various [2 + 2], [2 + 3], and [2 + 4] cycloadditions occur with **35** (Scheme 5). For example, four-membered rings are obtained from **35** and aldehydes or ketones;[63] the germaoxetanes **41** are highly stable, probably due to steric hindrance (at room temperature the rotation of the mesityl group is hindered, as shown by NMR). Generally, such heterocycles dimerize or decompose very easily to give germanones and alkenes. Diphenylimine reacts with germene **35** as a protic reagent to give **46** in nearly quantitative yield. With acetone the main reaction (90%) leads to **44**; the first step of the reaction is probably the formation of compound **43**, which cannot be observed. The intermediate undergoes a germanotropic rearrangement with formation of **44**. With azobenzene, a stable four-membered ring **47**[63] with a Ge–N–N linkage is obtained (Scheme 5). In this case also the steric hindrance plays a very important role for the stabilization; rotation of the mesityl group is hindered at room temperature, displaying six different methyl signals in the ^1H NMR (eq 15).



(14)

41

R′ = H, Ph

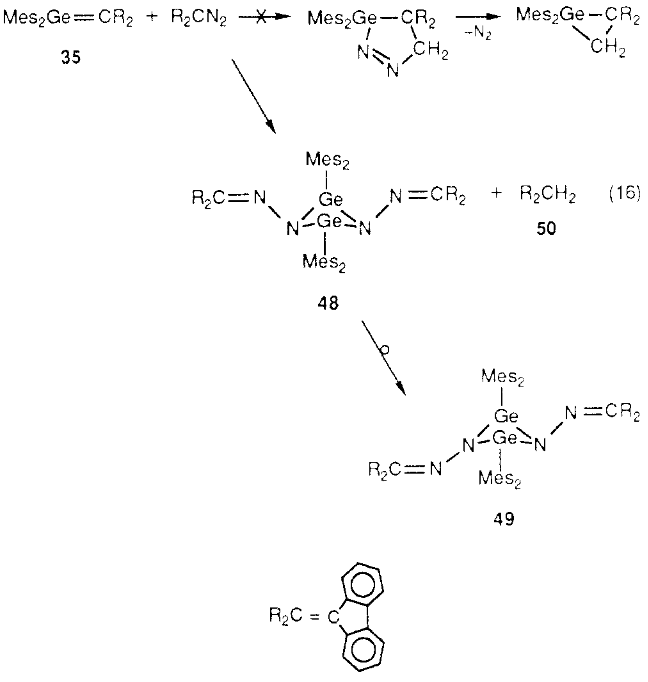


(15)

42

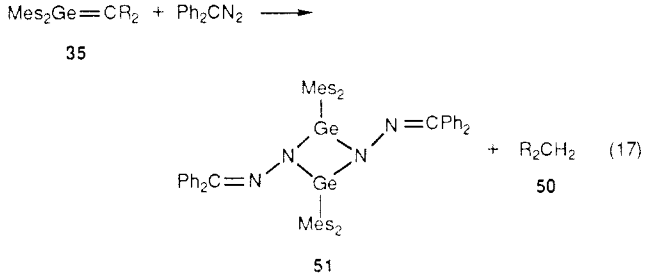
Nearly quantitative [2 + 3] cycloadditions have been observed with nitrones.[39] With 1,3-dienes[39] and α-ethylenic aldehydes and ketones,[63] [2 + 4] cycloaddition occurred (Scheme 5). Mass spectra (electron impact) of **41** and **47** show, besides the molecular peak, the two types of [2 + 2] decomposition: fragments with Ge–O or Ge=N double bonds are observed.

The reaction of diazofluorene with **35** gives quite surprising results.[65] It does not afford the expected three-membered-ring germacyclopropane (such heterocycles are still unknown and should be of great interest; due to a high strain, the Ge–C and C–C bonds should be very reactive), but the four-membered-ring cyclodigermazane **48**. The structure of **48** has been established by X-ray analysis, which demonstrates that the N=CR$_2$ moieties are in cis position. After 2 weeks in solution at room temperature, the thermodynamic trans isomer **49** is obtained. Fluorene **50** is also formed in this reaction (eq 16).



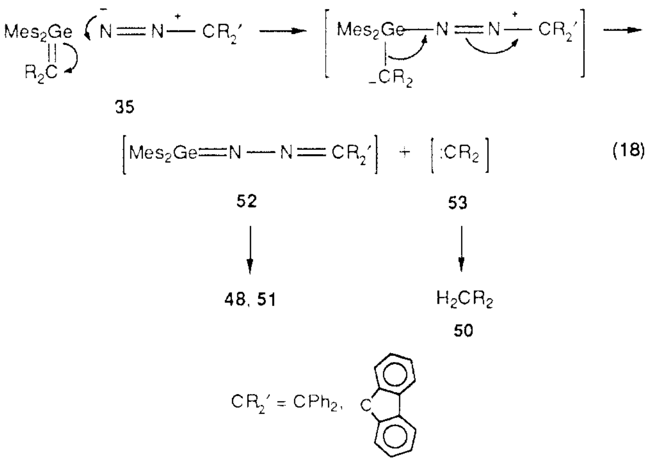
(16)

The reaction of **35** with diphenyldiazomethane[65] leads exclusively to germazane **51** and fluorene **50** (eq 17).



(17)

Among the mechanisms postulated, the most probable is given in eq 18. It seems reasonable to postulate the



(18)

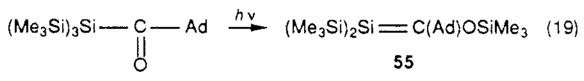
formation of the transient germanimine **52** followed by its dimerization. The presence of fluorene **50** can only be explained by abstraction of hydrogen from the solvent by a fluorenyl carbene intermediate **53**.

The structure of **48** is very close to that of germanimines obtained by Glidewell, which are stabilized by greater steric hindrance on germanium (two (Me$_3$Si)$_2$N instead of two mesityls) (see section IV).

(3) Silenes and Stannenes

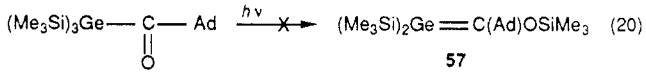
Large reviews have been devoted to compounds with silicon–carbon double bonds. Many transient silenes have been evidenced by trapping. Since the synthesis of the first stable silene, (Me$_3$Si)$_2$Si=C(OSiMe$_3$)(adamantyl) (**55**), by Brook in 1981[66a] (eq 19), some other stable silenes have been obtained, either by Brook (photolysis of acylsilanes[66b,67,68]) or by Wiberg (dehydrofluorination of fluorosilanes).[46,47,69]

Note that the photolysis of the adamantyl tris(trimethylsilyl)germane **56** (eq 20) does not give the expected germene **57**,[70] whereas a similar photolysis of the silicon analogue **54** gives rise to high yields of the isomeric silene **55**[66a] (eq 19).



$$(Me_3Si)_3Si-\underset{\underset{O}{\|}}{C}-Ad \xrightarrow{h\nu} (Me_3Si)_2Si{=}C(Ad)OSiMe_3 \quad (19)$$

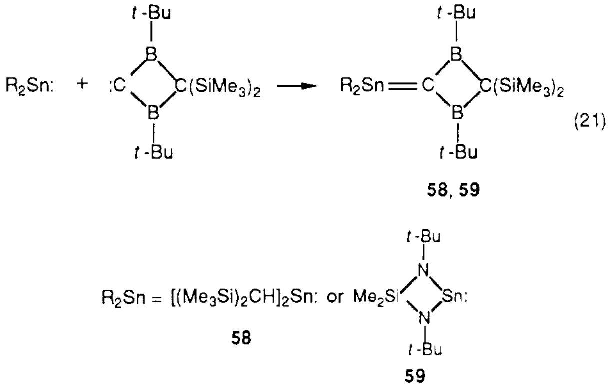
54 55



$$(Me_3Si)_3Ge-\underset{\underset{O}{\|}}{C}-Ad \xrightarrow[\times]{h\nu} (Me_3Si)_2Ge{=}C(Ad)OSiMe_3 \quad (20)$$

56 57

Recently, two stable stannenes, **58** and **59**, have been obtained by Berndt[38,71] in the reaction between stannylenes and the cryptocarbene **30** analogous to the synthesis of germenes (eq 21).



(21)

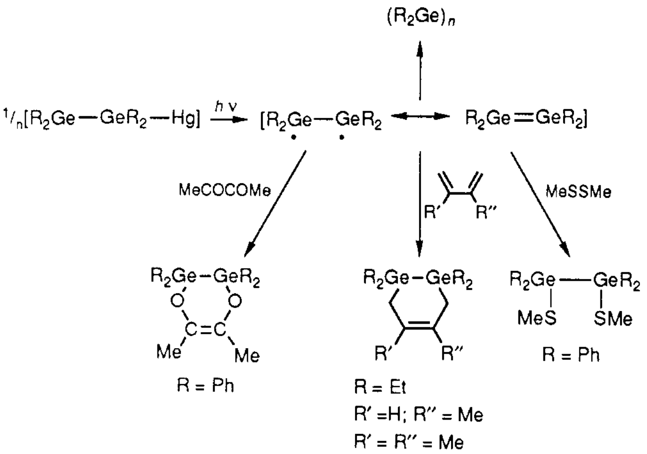
Compound **58** has been characterized by X-ray crystallography. The chemistry of such derivatives is not well developed, and only the addition of HCl onto the tin–carbon double bond has been performed.

III. Ge=Ge Species: Digermenes

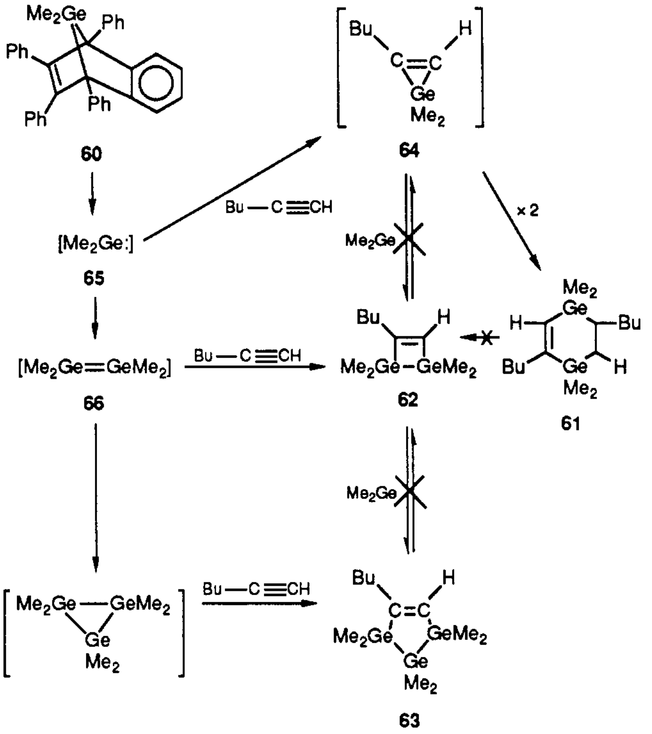
(1) Transient Digermenes

Digermenes are the heavier congeners of alkenes (>C=C<) and disilenes (>Si=Si<). Digermenes have been implicated as reactive intermediates in several reactions, but it was only in 1982 that solution spectra of a digermene, tetrakis(2,6-dimethylphenyl)digermene, were recorded.[72] We present here the different routes to transient digermenes, beginning with their charac-

SCHEME 6



SCHEME 7

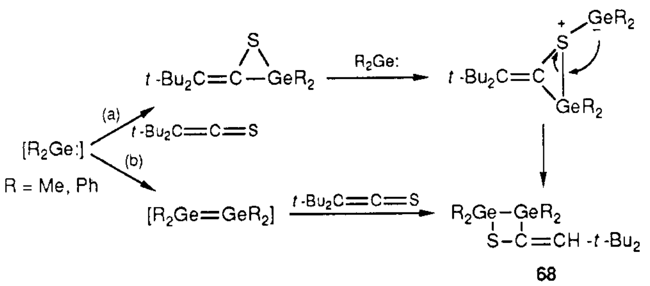


terization by chemical trapping, followed by the synthesis of stable digermenes with their structural data, and lastly theoretical aspects and calculations on such compounds.

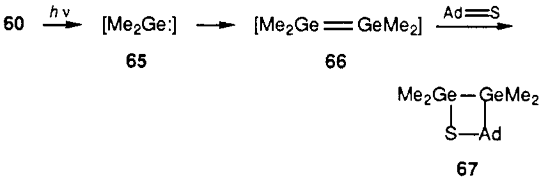
The first route to transient digermenes was the photolysis of polynuclear germylmercury compounds of the type $[-GeR_2GeR_2Hg-]_n$.[73,74] This reaction leads to a mixture of cyclopolygermanes $(R_2Ge)_n$, probably by intermediate formation of digermyl diradical R_2Ge–GeR_2,[73,74] which can be considered as the limiting form of digermene $R_2Ge{=}GeR_2$ and can be trapped by biacetyl,[73,74] dimethyl disulfide,[75] and dienes such as 2,3-dimethylbutadiene[75,76] and isoprene[76] (Scheme 6).

The dimerization of the germylene R_2Ge has been observed to lead to the corresponding digermene in some reactions.[32,33,77] For example, the thermolysis of germanorbornadiene **60** in the presence of butylacetylene leads to the three products **61**, **62**, and **63**.[77] Independent experiments have demonstrated that **62** cannot arise from **61**, **63**, or **64**. It is assumed that **62** is obtained by the rapid dimerization of Me_2Ge: (**65**) to give tetramethyldigermene (**66**) and subsequent cycloaddition with the alkyne (Scheme 7).

SCHEME 8



The formation of a digermene intermediate has also been postulated in the thermolysis of germanorbornadiene **60** in the presence of adamantanethione.[32,33] This reaction leads to the four-membered-ring 1,2-digermathietane **67**, probably via dimerization of germylene **65** in digermene **66** with subsequent [2 + 2] cycloaddition with adamantanethione[32,33] (eq 22). The other

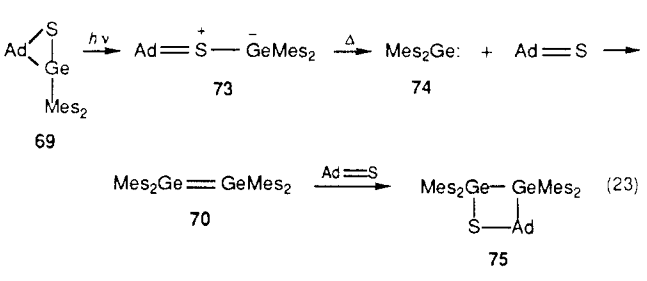


$$60 \xrightarrow{h\nu} \underset{65}{[Me_2Ge:]} \longrightarrow \underset{66}{[Me_2Ge{=}GeMe_2]} \xrightarrow{Ad{=}S} \underset{67}{Me_2Ge{-}GeMe_2(S{-}Ad)} \quad (22)$$

Ad = adamantyl

products obtained in this reaction probably arise from a germanethione intermediate (see section VI). The formation of dimethylgermylene (**65**) from germanorbornadiene **60** has been proved unambiguously by Ando.[78] When a solution of **60** cooled at 77 K was irradiated with a low-pressure mercury lamp, the matrix became intensely yellow and a broad electronic absorption band with a maximum of 420 nm was observed. The electronic spectra of Me_2Ge: had been previously reported to have a λ_{max} = 430 nm, in good agreement with the results of Ando.[78] Convincing evidence is provided by the result of a chemical trapping experiment of **65** with dimethylbutadiene, leading to the formation of the corresponding germacyclopentene.[78] Reaction between **60** and di-*tert*-butylthioketene leads also to digermathietane **68**. In this case the authors[80] report that **68** is more likely obtained via route a than via route b involving a digermene intermediate $R_2Ge{=}GeR_2$ (Scheme 8).

The matrix isolation technique has been used widely for the observation of the reactive species. For example, in the irradiation of thiagermirane **69** in 3-methylpentane at 77 K with a low-pressure mercury lamp, a new band at 690 nm appeared, indefinitely stable at 77 K[33] (eq 23). The careful annealing and recooling of the matrix led to the disappearance of this band and the formation of a new one at 406 nm, which was assigned to tetramesityldigermene (**70**). On the basis of results obtained in the photolysis of oxa(or thia)silirane **71**[81] (eq 24), the authors assign the band at 690 nm to the germathiocarbonyl ylide **73**, which decomposes thermally to dimesitylgermylene (**74**) with subsequent dimerization into digermene **70**. This digermene reacts with adamantanethione to yield **75**[33] (eq 23).



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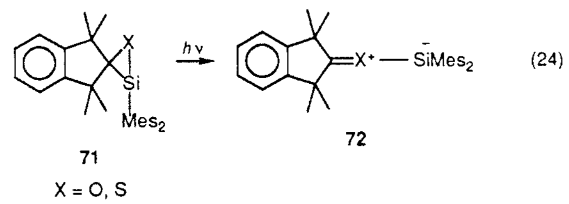
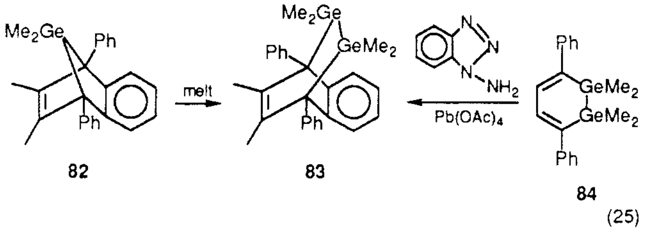


(24)

Pyrolysis of the six-membered-ring 1,2-tetraethyldigerma-4-cyclohexene **76** at 500 °C under 10^{-2} Torr leads in the absence of trapping reagent to polymers and also to 2- and 3-germacyclopentenes **77** and **78**[82] (Scheme 9). The tetraethyldigermene has been detected by its trapping with 1,4-diphenylbutadiene or benzaldehyde. In this last case, the four-membered ring **79** decomposes to germene and germanone $Et_2Ge{=}O$. Germene **80** can then react with an excess of benzaldehyde to give finally germoxanes **81**[82] (Scheme 9).

Similar pyrolysis of the disila analogue of **76** yields disilenes, which can be trapped by conjugated dienes or aldehydes.[82] It must be noted that the [4 + 2] cycloreversion is easier with the digermacyclohexene (from 400 °C) than with its disila isologue (between 500 and 600 °C).

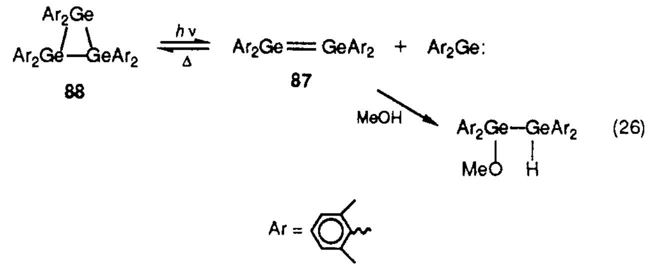
In the molten state, 7-dimethylgermanorbornadiene **82** acts as a powerful germylene scavenger,[83,84] competing successfully with the rapid polymerization of germylene by insertion into the highly strained germanium–carbon bond to form benzodigermabicyclooctadienes **83**.[83,84] The heterocycle **83** has also been synthesized[85] from digermacyclohexadiene **84** and benzyne (eq 25). Such heterocycles **83** are by



(25)

thermolysis at ca. 170 °C very good precursors of tetramethyldigermene, which is found to be an active dienophile and can be trapped by anthracene[84,85] and silacyclopentadiene.[85] Whereas reaction of tetramethyldigermene (**66**) with diphenylacetylene and bis(trimethylgermyl)acetylene failed,[85] a [2 + 2] cycloaddition is observed with the cyclic acetylene **85** to give the digermacyclobutene **86**.[83] Although highly strained, **86** is thermally stable and was characterized by X-ray analysis (Scheme 10).

One of the most important sources of digermenes is the photolysis of three-membered-ring trigermiranes >Ge–Ge–Ge<.[10,20,33,72,86,87,89] This route gave the first metastable digermene **87**[72] but the slow photolytic conversion from **88** and concomitant photoinduced polymerization of **87** prevented its isolation. Nevertheless, **87** was clearly characterized spectroscopically by UV and proton NMR and chemically by trapping with methanol (eq 26).

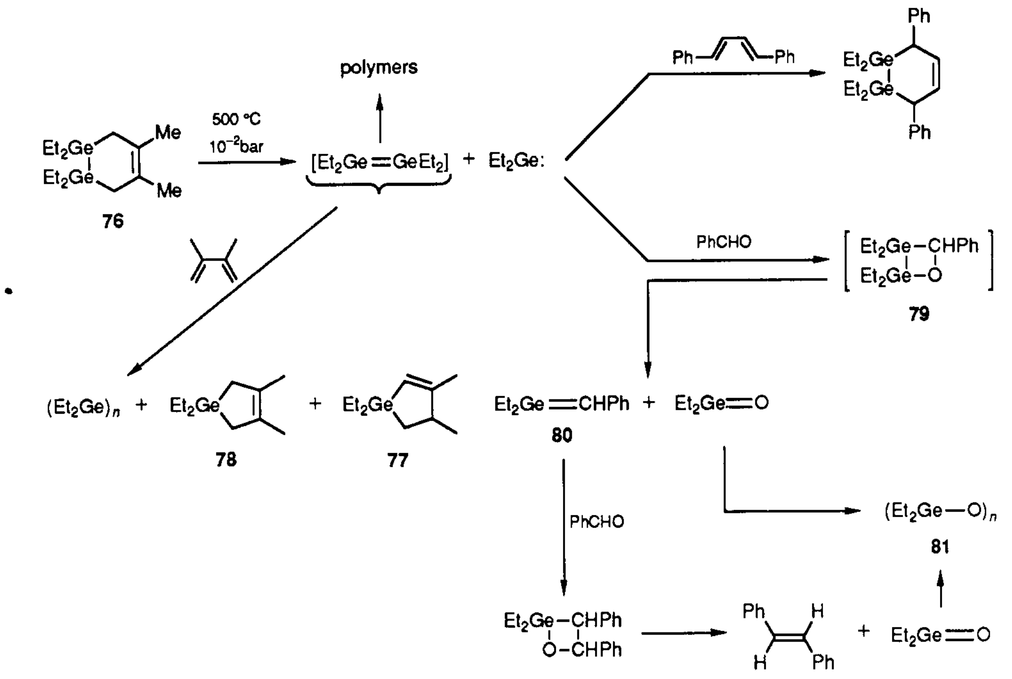


(26)

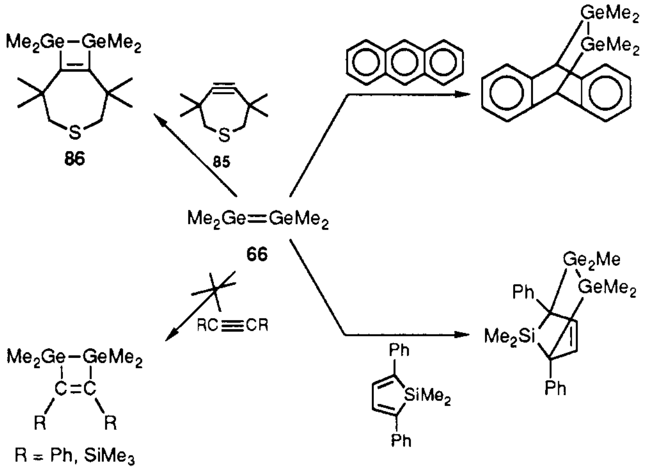
During photolysis or mild thermolysis of a solution of hexamesitylcyclotrigermane (**89**) in the absence of trapping reagent, the solution turned yellow with a maximum at 410 nm, which was assigned to digermene **70**.[78] After irradiation or thermolysis, **89** was recovered almost quantitatively, suggesting that the decomposition of **89** into digermene **70** and germylene **74** may be a reversible reaction.[88] Photolysis of **89** in the presence of adamantanethione leads to the corresponding three- and four-membered rings,[33] due to the reaction of adamantanethione with germylene **74** and digermene **70**. Thermolysis of **89** at 80 °C in the presence of paraformaldehyde or phenylacetylene gives the corresponding four-membered ring oxadigermetane or digermetene in good yield.[88] Only the digermene **70** has been trapped in these two reactions. In the case of dimethylbutadiene and thiobenzophenone (thermolysis)[88] or sulfur and selenium (photolysis),[86] both products resulting from trapping of digermene **70** and germylene **74** have been obtained. With sulfur and selenium, the formation of **90** can be explained by the transient formation of germanethione or germaneselenone **91** (Scheme 11).

Although it is well-known that seleniranes >C–C–Se are generally unstable molecules (they decompose easily to olefins with the extrusion of selenium), selenadigermirane **92b** is thermally very stable and does not decompose when heated to its melting point (217–219 °C).[86a] A great difference is observed between the chemical behavior of alkenes and their heavier homologues. Under normal conditions, alkenes do not react with sulfur or selenium, but disilenes[90] or digermenes react very easily to form stable three-membered adducts.[86a] Note that other [2 + 1] cycloadditions have recently been observed between sulfur and selenium and doubly bonded derivatives of main-group elements such as diphosphenes,[91–93] diarsenes,[94] phosphaarsenes,[95] or germaphosphenes.[96] The structure of **92a** has been proved by X-ray analysis; **92a** presents surprisingly some character of a π complex.[86a] The Ge–Ge bond length (2.376 Å) is remarkably shorter than the normal bond length (2.44 Å). This is not a characteristic feature of three-membered rings because hexakis(2,6-dimethylphenyl)cyclotrigermane has very long Ge–Ge bonds (2.53–2.54 Å). Also surprising is the nearly planar arrangement around germanium. The sum of the bond angles Ar–Ge–Ge′, Ar′–Ge–Ge′, and Ar–Ge–Ar′ around each germanium is 357.3 and 356.7°, respectively, close to the expected 360° for a planar sp^2 germanium. According to Dewar's model of metal–olefin bonding,[97,98]

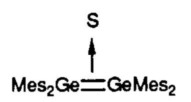
SCHEME 9



SCHEME 10



Ando suggested that **92a** has some of the character of π complex A. Recently, such similar structures have



$$\overset{S}{\uparrow}\atop{Mes_2Ge{=}GeMes_2}$$

A

been reported for other three-membered rings such as thiadisilirane,[90] oxadisilirane,[99] disilirane,[100] and germathiaphosphirane[96] (see section V). The theoretical investigation of Grev[101] on three-membered rings containing two silicon atoms, $\overline{>Si{-}Si{-}X}$, supports these results.

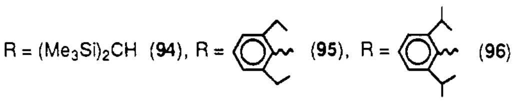
The photolysis of cyclotetragermanes **93**[75] is also a route to digermenes (or to the corresponding biradicals) by successive α elimination of germylene. Trapping by dimethyl disulfide proves unambiguously the mechanism of this reaction (Scheme 12). Cyclopentagermanes give under UV irradiation the same type of decomposition with the final formation of the digermene, but much less rapidly.[75]

(2) Stable Digermenes

(a) Synthesis and Reactivity

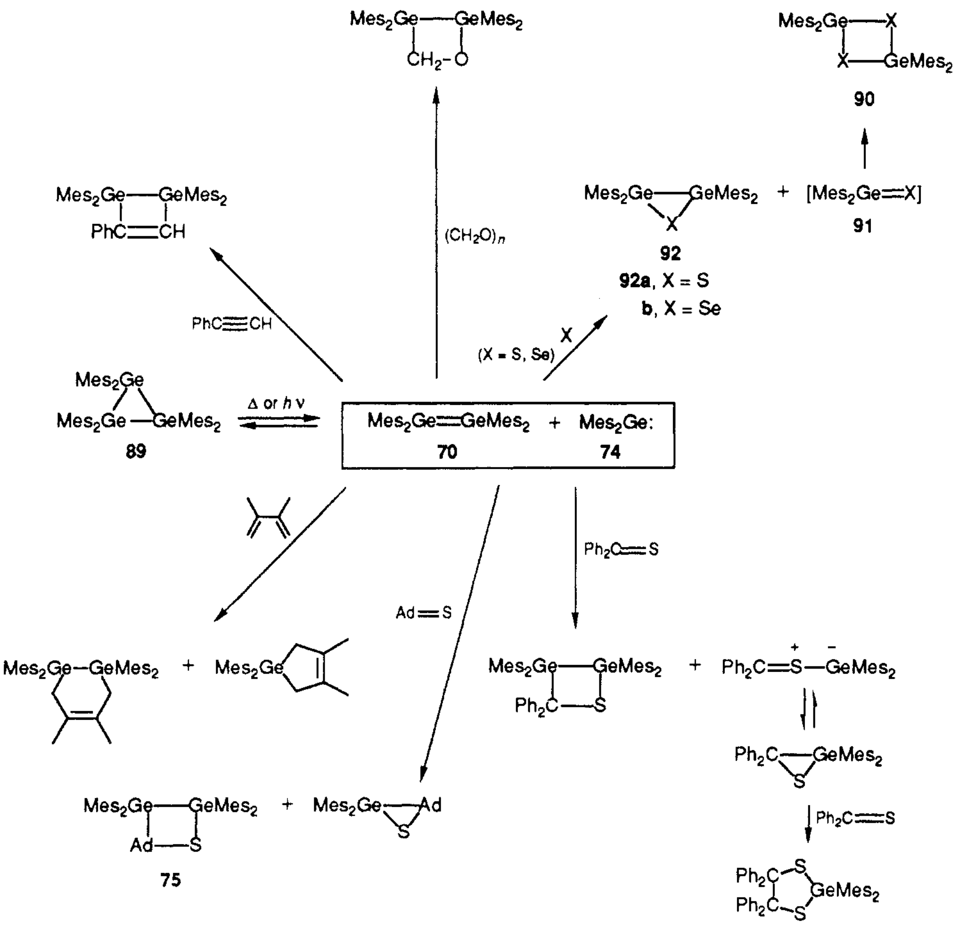
Two compounds with a germanium–germanium double bond, $R_2Ge{=}GeR_2$ (R = bis(trimethylsilyl)methyl (**94**),[102,103] R = 2,6-diethylphenyl (**95**)[10,87,104]) have been characterized in the solid state by X-ray analysis,[10,102,103] but only **95** retains its digermene structure in solution,[10,87] whereas the other disproportionates into two germylenes.[102] Another digermene stable in solution, **96**, (R = 2,6-diisopropylphenyl) has been recently obtained[89] (eq 27).

$$R_2Ge{=}GeR_2 \qquad (27)$$

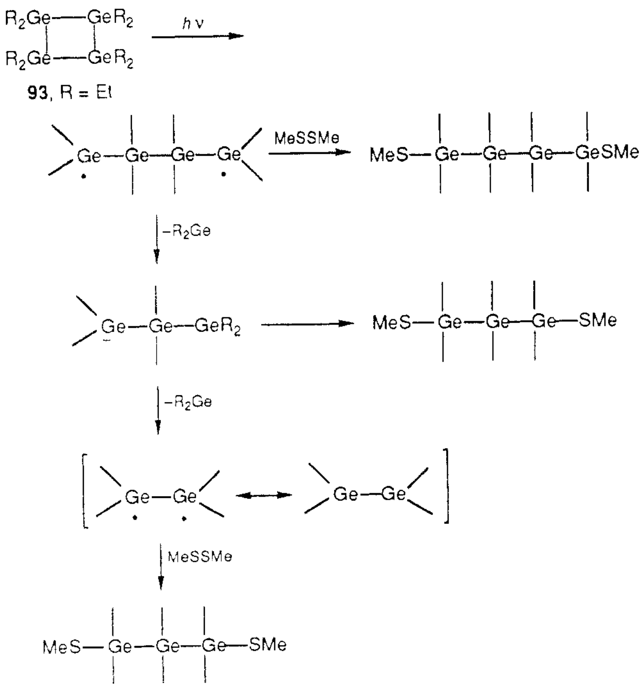


Compound **95** is obtained in >90% yield by irradiation of cyclotrigermane **97**.[10,87,104] These appear in the form of thermally stable yellow air- and moisture-sensitive crystals. The mechanism of the formation of **95** and its photostability with respect to fragmentation to **98** were investigated. Irradiation of cyclotrigermane **97** and of **99** was performed under different conditions.[89] It appears that photolysis of **99** gives germylene **98**, which thermally dimerizes after irradiation to digermene. In the photolysis of cyclotrigermane **97**, both germylene and digermene are observed at the beginning of irradiation by NMR. Prolonged irradiation afforded exclusively germylene **98**, which can be trapped by 2,3-dimethylbutadiene or methanol[89] (Scheme 13). The structure of **86** was determined by X-ray analysis[10] (see below) as well as chemically. Addition of methanol gives the addition product **100**[10,87] and proves unambiguously the digermene structure. [2 + 1] cycloaddition reactions have been observed with selenium,[105]

SCHEME 11

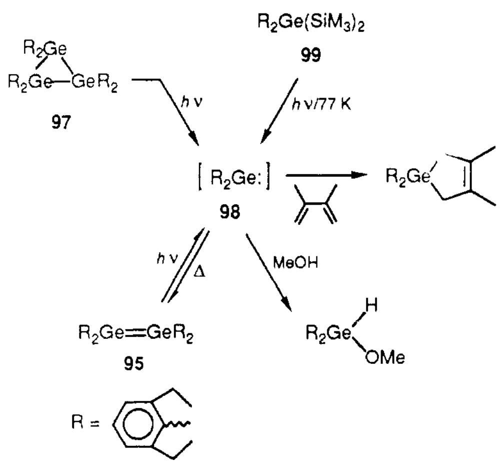


SCHEME 12

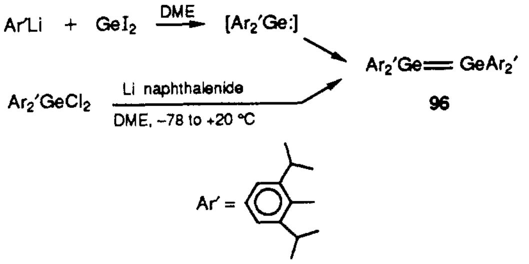


[2 + 2] with acetone[105] and phenylacetylene,[105] and [2 + 3] with diazomethane[20,105] and phenyl azide.[20,105] In these two last cases three-membered rings **101** and **102** are obtained after elimination of nitrogen. Note that in the reaction with acetone, only the [2 + 2] cycloadduct is obtained[105] and no ene-type products are observed (Scheme 14).

SCHEME 13



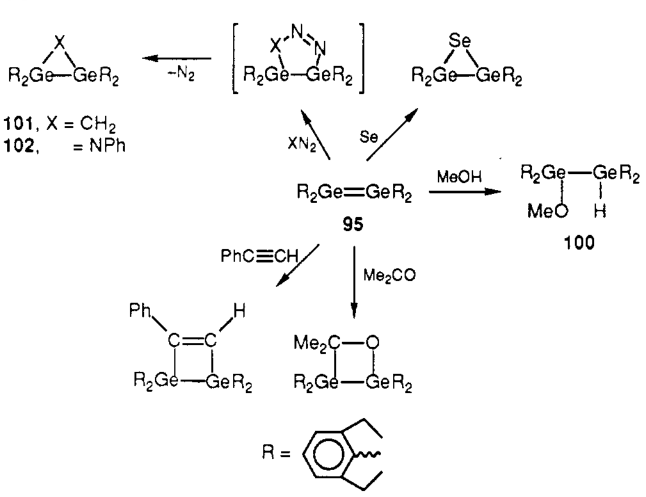
Contrary to **95**, **96** can be obtained directly from the corresponding dichlorogermane Ar'_2GeCl_2, by addition of lithium naphthalenide at low temperature (eq 28).



(28)

After elimination of naphthalene in vacuo, the usual

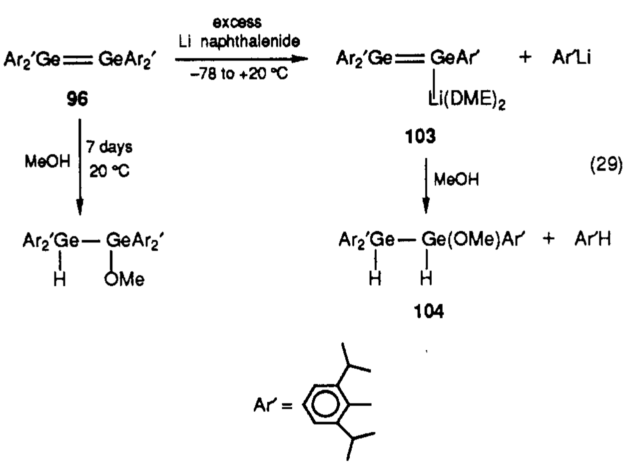
SCHEME 14



workup affords **96** in 25% yield (the yield before purification is estimated to be 65% by NMR). The digermene **96** can also be obtained in low yield (10%) by the reaction of GeI_2 with 2 equiv of (2,6-diisopropylphenyl)lithium, with the transient formation of the germylene Ar'_2Ge, followed by dimerization.

The steric hindrance in this molecule is clearly demonstrated by NMR, which shows two types of isopropyl groups. This phenomenon is temperature independent in toluene from −80 to +100 °C. The hindered rotation of the aryl groups along the Ge–C axis is certainly responsible for the nonequivalence of the isopropyl groups. In contrast, the spectrum of **95** at room temperature has only one type of ethyl group but can be induced to show two types of ethyl groups upon cooling to below −80 °C.

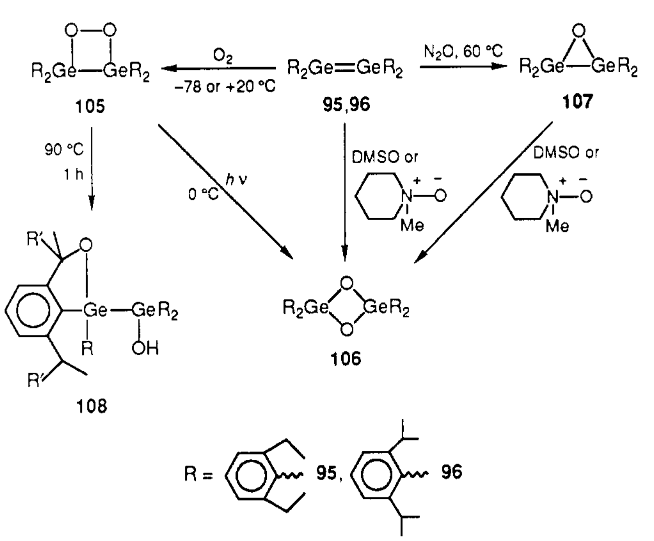
Due to the very large Ar′ groups, the Ge–Ge double bond of **96** is effectively protected from attack by external reagents. For example, addition of methanol to **96** proceeds only to 33% completion in 7 days whereas this reaction is complete in 30 min at room temperature for **95**. Addition of an excess of lithium naphthalenide results in a totally unexpected reaction, with the formation of digermenyllithium (DME) complex **103**, which gives **104** after methanolysis (eq 29).



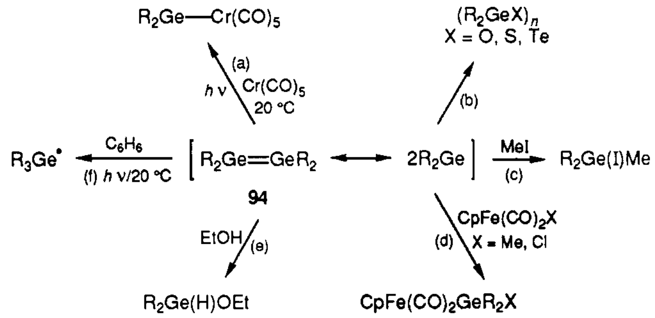
(29)

Oxygenation of digermenes **95** and **96** gives, depending on the oxidant used and on the experimental conditions, 1,2-digermadioxetanes **105**, 1,3-cyclodigermoxanes **106**, or digermoxirane **107** derivatives[106] (Scheme 15). Exposure to oxygen leads to **105**, which upon heating at 90 °C is isomerized to **108**. Photolysis of **105** yields **106**. Three-membered-ring **107** is obtained with nitrous oxide. Addition of DMSO or *N*-methylmorpholine *N*-oxide to **95**, **96**, and **107** affords the cyclodigermoxane **106**. The structures of **105a** and **106a** (R = 2,6-diethylphenyl) have been proved by X-ray analysis[106] (Scheme 15). The skeletal geometry of **106a** is square with a Ge–Ge distance of 2.617 (1) Å, longer than the Ge–Ge normal bond length (2.46 Å). This is contrary to the case of its silicon analogue $[Mes(t\text{-}Bu)SiO]_2$;[107] in this compound the Si–Si distance is shorter than a normal Si–Si bond length.

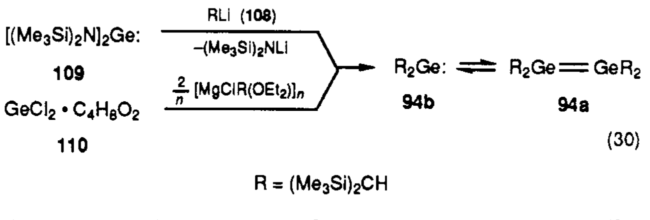
SCHEME 15



SCHEME 16



Digermene **94** is prepared from germylene **109** by reaction with bisyllithium, $(Me_3Si)_2CHLi$ (**108**) or from dichlorogermylene–dioxane complex **110** and Grignard reagent[109a] (eq 30). Contrary to **95**, which is clearly dimeric, the digermene **94** disproportionates very easily in solution into two singlet germylenes.[102,103] However, in the crystalline state **94** was shown to be dimeric by X-ray crystallography[102,103] (see X-ray below). The chemical properties of **94** are those of the monomer R_2Ge:. It reacts as a Lewis base ((a) in Scheme 16), a substrate for valence expansion to yield a tetravalent germanium adduct ((b)–(e)), or a substrate for disproportionation ((f)).[102] It is also evident that $R_2Ge{=}GeR_2$ resembles $R_2Sn{=}SnR_2$: in these two compounds the



(30)

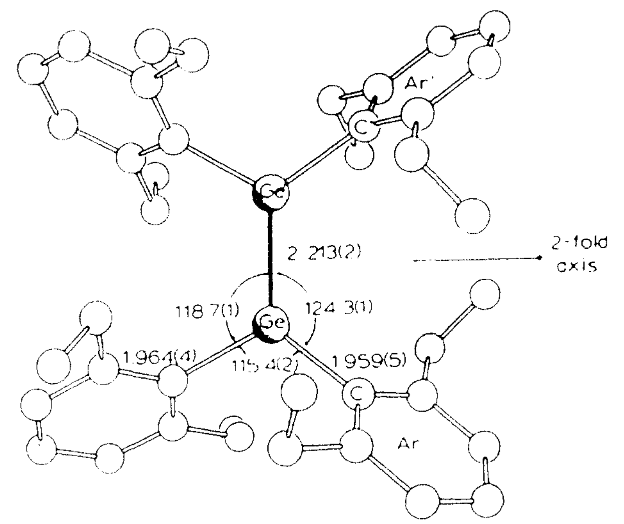


Figure 3. ORTEP view of **95** (reprinted from *Tetrahedron Lett.* 1984, *25*, 4191; copyright 1984 Pergamon Press Inc.).

M=M bond is exceedingly labile. Note the great difference of reactivity in solution between **95** and **94** toward alcohols; in this reaction **94** behaves as a germylene[103] and **95** as a digermene.[10,87] The structural integrity of the digermene species (i.e., dimeric or monomeric) in solution seems to be very sensitive to substituent effects. In the gas phase the germylene **94b** is also observed by mass spectrometry,[108,109c] photoelectron spectroscopy,[108,109c] and gas electron diffraction.[109b]

The monomeric nature of **94** in solution contrasts with that of its silicon analogue, which is dimeric both in solution and in the solid state.

(b) Physicochemical and Theoretical Studies

X-ray Structures and Theoretical Aspects. The differences in chemical behavior between **94** and **95** can be understood from their X-ray structures (Figures 3 and 4). The Ge=Ge double-bond length is very long in **94**,[102,103] which explains its easy cleavage. The shortening in relation to the standard germanium–germanium bond (2.465 Å in $(Ph_2Ge)_4$,[111] 2.463 and 2.457 Å in $(Ph_2Ge)_6$[112]) is only 4% in **94** but 8% in **95**, which corresponds to the standard shortening for doubly bonded main-group elements. The germanium environment in both **94** and **95** is intermediate between pyramidal and planar. Theoretical studies using various basis sets[103,113-115] predicted a trans-bent geometry with short Ge–Ge distance (2.30[114] and 2.325 Å[113]) and important fold angle θ (40[114] and 38.9°[113]) (Table 5). The bonding occurring in $H_2Ge{=}GeH_2$ has been described as two semipolar bent bonds between two singlet germylenes[113] (eq 31).

(31)

The ab initio molecular orbital calculations with better than double ζ basis sets on the model compounds M_2H_4 (M = Ge, Sn) show that trans-folded equilibrium structures are more stable than planar by 3–4 kcal/mol for germanium[103,113] and 6 kcal/mol for tin. The structures predicted by calculations (semipolar bent bond between two singlet germylenes) correspond well to the digermene **94** obtained by Lappert, except for the Ge=Ge double bond, which is found experimentally longer. The X-ray structure of **95**, however, displays a slightly different structure closer to that of alkenes. The M=M dissociation energy is calculated to be 30 kcal/mol for germanium (22 kcal/mol for tin).[103] These energies are about half the experimental >M–M< single-bond dissociation energies of H_3GeGeH_3 or Me_3GeGeM_3.[103,109b] The decreasing strength of M–M bonding in the series M_2X_4 with increasing atomic number of M as well as the increasing stability of the trans-folded relative to planar structures is attributed to the increasing inertness of the electron lone pair in the MX_2 monomer, which in turn is reflected in an increasing singlet → triplet excitation energy.[103]

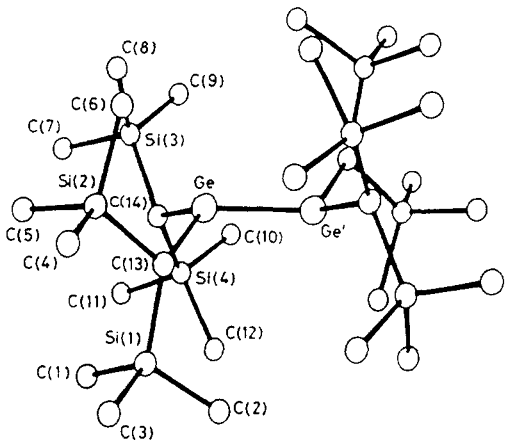
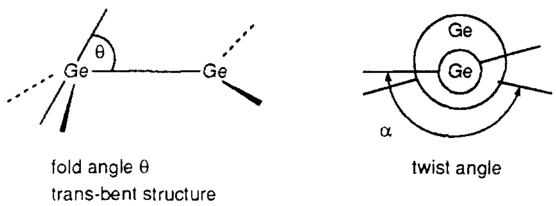


Figure 4. ORTEP view of **94** (reprinted from *J. Chem. Soc., Chem. Commun.* 1984, 480; copyright 1984 Royal Society of Chemistry).

TABLE 5. Some Structural Parameters of 94 and 95



compd	d(Ge=Ge), Å	shortening	fold angle θ, deg	twist angle α, deg	sum of angles on Ge, deg
95	2.213 (2)	8%	15	11	358.4
94	2.445	4%	32	0	348.5

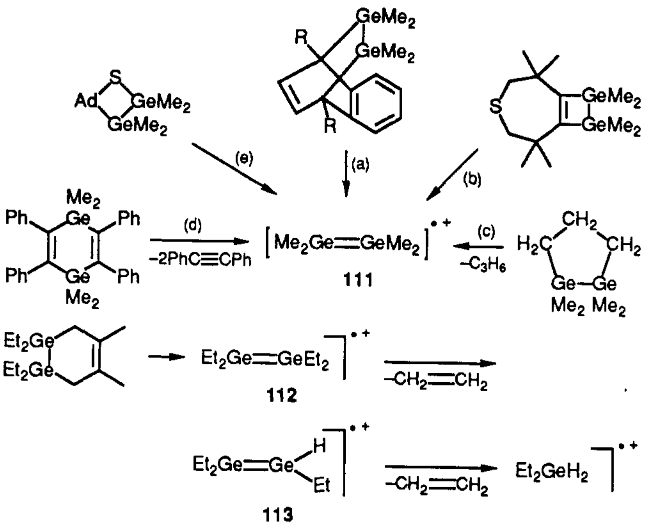
Ab initio calculations using pseudopotentials have been carried out on digermene ($H_2Ge{=}GeH_2$) and its germylgermylene isomer ($HGeGeH_3$) at both SCF (double ζ + d basis sets) and CI levels. The digermene is predicted more stable than the germylene by 5 kcal/mol.[113]

IR, Raman, UV, and Mass Spectroscopy. The UV absorption band of the Ge=Ge double bond was observed when the matrix containing dimesitylgermylene was annealed: a yellow coloration appeared due to tetramesityldigermene ($Mes_2Ge{=}GeMes_2$) (λ_{max} = 406 nm at 77 K).[78] This absorption band is identical with that obtained from the photolysis of hexamesitylcyclotrigermane giving tetramesityldigermene.[33] In the case of $Ph_2Ge{=}GePh_2$, λ_{max} is observed at 320 nm.[116] A strong Raman band at 300 cm^{-1} attributed to ν(Ge–Ge) was observed in crystalline **94**,[103] in good agreement with calculations (286 cm^{-1} [55]).

TABLE 6. Observed and Calculated Skeletal Vibrations of the Isolated Tetramethyldigermene $Me_2Ge{=}GeMe_2$ (cm^{-1})

	Raman			IR	
	obsd			obsd	
assignment	Ar	N_2	calcd	Ar	calcd
ν(Ge–C)	591	589	588	598	593
	580	580	576	568	564
ν(Ge–Ge)	404	405	401		
δ(GeGeC)	235	234	232		
δ(CGeC)	200	198	206		

SCHEME 17[a]



[a] a, R = H,[84] Ph;[85] b, ref 83a; c, ref 117; d, ref 118; e, ref 33.

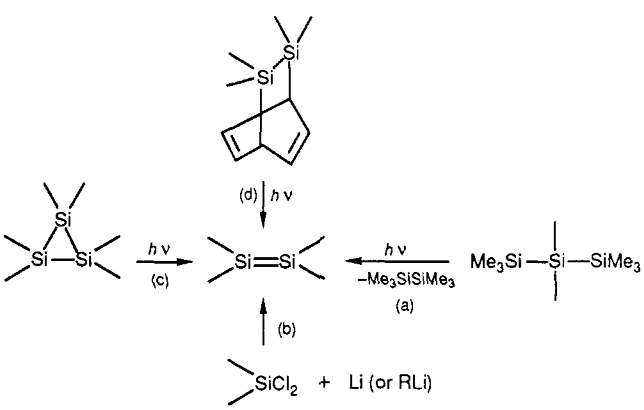
Tetramethyldigermene ($Me_2Ge{=}GeMe_2$) has been isolated in argon and nitrogen matrices[84] by thermolysis of germanorbornadiene 82 in the solid state or melt (see eq 25). IR and Raman data have been obtained in matrices at 5 K (see Table 6). Whereas a planar model gave insufficient approximations, the trans-bent geometry in accordance with the theory[113,115] led to the best agreement with the measured frequencies. The ν(Ge=Ge) (404 cm^{-1}) is much higher than in the case of the single-bonded digermane $Me_3Ge{-}GeMe_3$ (275 cm^{-1}). This means that $Me_2Ge{=}GeMe_2$ can really be written with a double bond like an alkene. It is bent, and dipolar or biradical forms give, if any, only minor contributions.[84]

The tetramethyldigermene ion **111** and the tetraethyl- and triethyldigermene ions **112** and **113**[82] have been observed by mass spectroscopy of various substrates. These fragmentations are consistent with the results of thermolysis of parent compounds: in all cases digermenes were relatively easily generated and could be chemically evidenced by in situ trapping[82] (Scheme 17).

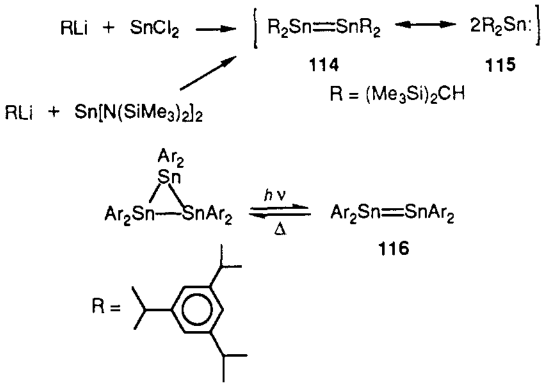
(3) Disilenes and Distannenes

Many transient disilenes have been generated by various methods and evidenced by trapping.[4] The first stable disilene was prepared by West in 1981[119] by photolysis of an acyclic trisilane leading to the intermediate formation of a silylene and dimerization (route a). Other routes afford stable disilenes, such as the photolysis of cyclotrisilanes (c) or of bicycles with a Si–Si bridge (d), reaction of dichlorosilanes with lithium or lithio compounds (b), and redistribution of other disilenes (Scheme 18). Various groups on silicon were found to stabilize disilenes R(R′)Si=Si(R′)R (R, R′ = $(Mes)_2$;[119,120] $(2,6\text{-}Me_2C_6H_3)_2$;[121a] $(2,6\text{-}Et_2C_6H_3)_2$;[10,87,121b] t-Bu, Mes;[122,123] $(Me_3Si)_2N$, Mes;[124] $(2,4,6\text{-}i\text{-}Pr_3C_6H_2)_2$;[125] $[(Me_3Si)_2CH]_2$.[126] Some other disilenes are marginally stable in solution when substituted by a less bulky group: R (R′): $(t\text{-}BuCH_2)_2$;[127] $t\text{-}Bu_2$;[127–129] $(Et_2CH)_2$;[130] $(Me_3SiCH_2)_2$;[131a] $i\text{-}Pr_2$;[132b] $(Et_3Si)_2$;[132] Mes, Ad;[133] $i\text{-}Bu_2$;[131a] $s\text{-}Bu_2$;[131a] t-Bu, Pr;[131a] t-Bu, Me.[131a]

SCHEME 18



SCHEME 19



X-ray structures show a shortening of about 8% in relation to the standard silicon–silicon single bond and an alkene-like structure with planarity around the double bond.[2b,4] The chemical behavior of such derivatives is well-known, and many insertion reactions and cycloadditions have been performed.[2b,4]

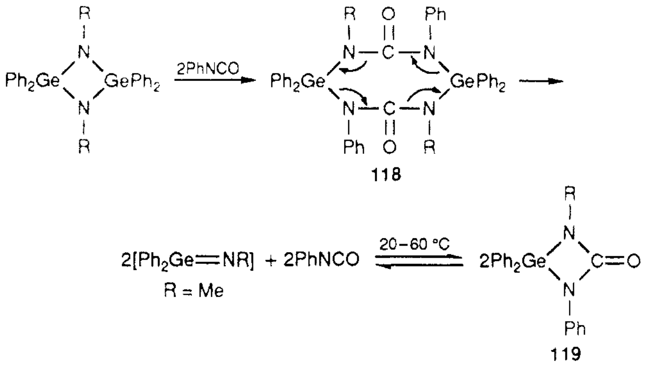
In the case of distannenes $R_2Sn{=}SnR_2$, two types of compounds with a double bond between two tin atoms have been obtained, like for digermenes: compound **114**, obtained by Lappert, has a distannene structure only in the solid state, as shown by X-ray analysis,[103,114] with a very small shortening of the tin–tin double bond. In solution the reactivity of **114** corresponds to the reactivity of stannylene **115** (Scheme 19). Another distannene **105**, obtained by photolysis of a cyclotristannane, has recently been described by Masamune[134] (Scheme 19) and retains its distannene structure in solution: the ^{119}Sn NMR spectrum displays a signal characteristic of an sp^2-hybridized tin (+427 ppm/Me_4Sn) with a very large $^{119}Sn{-}^{117}Sn$ tin–tin coupling.

IV. Ge=N Species: Germanimines

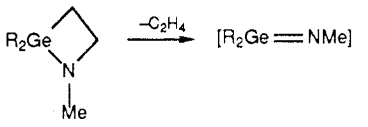
(1) Transient Germanimines

The formation of germanimine intermediates

SCHEME 20



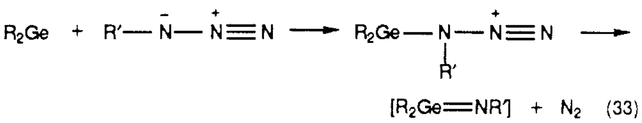
$R_2Ge{=}NR'$ was first observed by a β-elimination process from unstable germaazetidine **117**^{6,135,136} (eq 32).



(32)

117

They are also formed by the action of phenyl or methyl azides on germylenes^{137} (eq 33). The direct interaction



$$R_2Ge + R'{-}\overset{-}{N}{-}\overset{+}{N}{\equiv}N \longrightarrow R_2Ge{-}\underset{R'}{N}{-}\overset{+}{N}{\equiv}N \longrightarrow [R_2Ge{=}NR'] + N_2 \quad (33)$$

of a germylene with a nitrene also leads to germanimines.^{6,137} Like silanimines the germanimines can also be generated by photolysis of triorganogermanium azides^{6,139} (eq 34). Germanimines have been quantitatively trapped by pinacol.^{6,139}

$$R_3GeN_3 \xrightarrow[-N_2]{h\nu} [R_2Ge{=}NR] \quad (34)$$

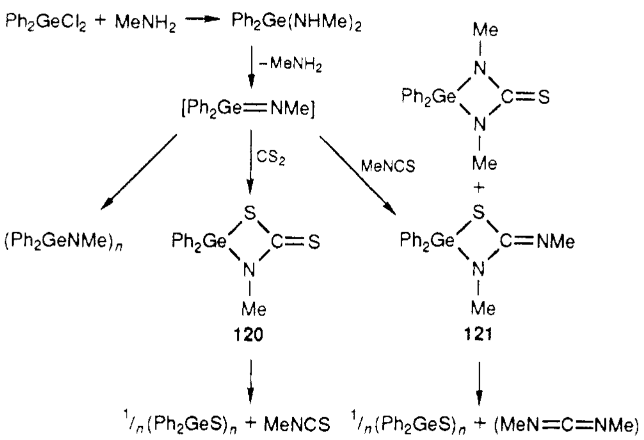
Another route to germanimines is via the reaction of 2 mol of phenyl isocyanate with 1 mol of cyclodigermazane leading to diadduct **118**, which decomposes through successive eliminations to a germanimine stabilized by dipole–dipole interaction with phenyl isocyanate and thence to equilibrium with an unstable germaoxodiazetidine **119**^{6,140} (Scheme 20).

Studies of ring opening of cyclogermazanes $(R_2GeNR')_n$ (n = 2, 3)^{6,140,141} and chlorocyclotrigermazanes $(Cl_2GeNR)_n$ (n = 2, 3)^{142} induced by Lewis bases (Et_3N, HMPA) or Lewis acid ($ZnCl_2$, $M(CO)_6$, $M(CO)_5{\cdot}THF$ (M = Cr, W) show the existence of an equilibrium between cyclogermazanes and germanimines. The 1,3-cycloaddition with nitrones is proposed as chemical evidence of germanimine formation in this equilibrium.$^{6,140-142}$

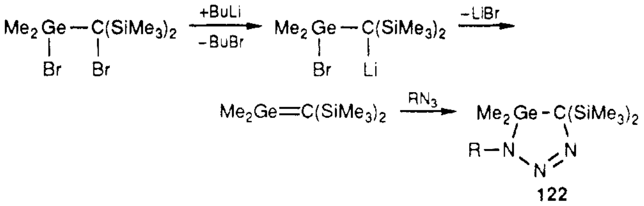
It is prossible to characterize germanimine intermediates in the ammonolysis of diphenyldichlorogermane by trapping (under conditions in which the cyclogermazane does not react) of the germanimine with CS_2 to yield germathiaazetidine **120**, which then decomposes to $Ph_2Ge{=}S$ and MeNCS. Subsequent reaction of MeNCS on germanimine is also observed with formation of germathiaazetidine **121**^{6,140} (Scheme 21).

The formation of germanimine $Ar_2Ge{=}NPh$ (Ar = (2,6-diethylphenyl)) is postulated in the photodecomposition of the azadigermiridine $Ar_2\overline{GeGe(Ar_2)N}Ar$.^{20}

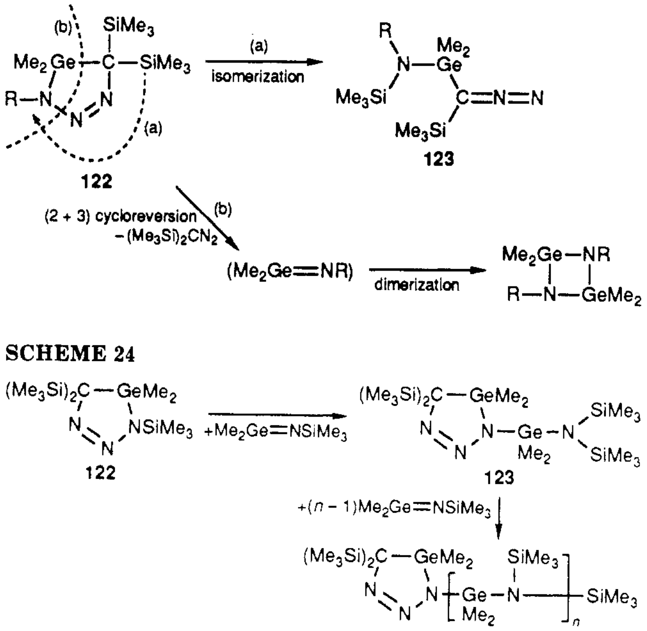
SCHEME 21



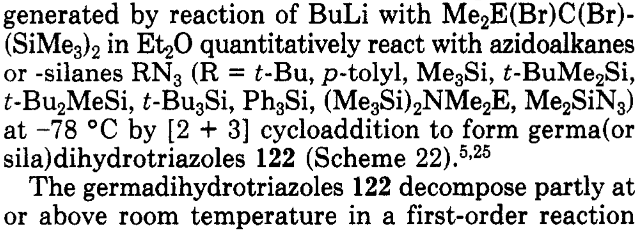
SCHEME 22



SCHEME 23



SCHEME 24

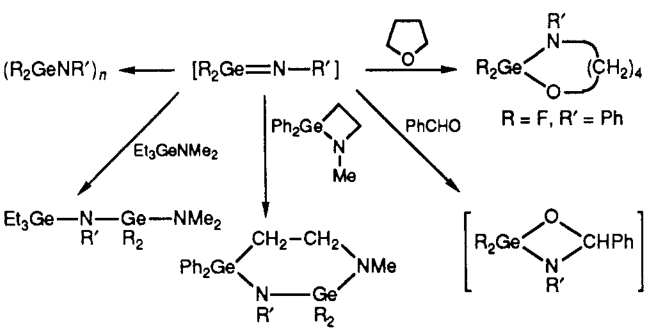


Germene and silene $Me_2E{=}C(SiMe_3)_2$ (E = Ge, Si) generated by reaction of BuLi with $Me_2E(Br)C(Br)(SiMe_3)_2$ in Et_2O quantitatively react with azidoalkanes or -silanes RN_3 (R = t-Bu, p-tolyl, Me_3Si, t-$BuMe_2Si$, t-Bu_2MeSi, t-Bu_3Si, Ph_3Si, $(Me_3Si)_2NMe_2E$, Me_2SiN_3) at −78 °C by [2 + 3] cycloaddition to form germa(or sila)dihydrotriazoles **122** (Scheme 22).^{5,25}

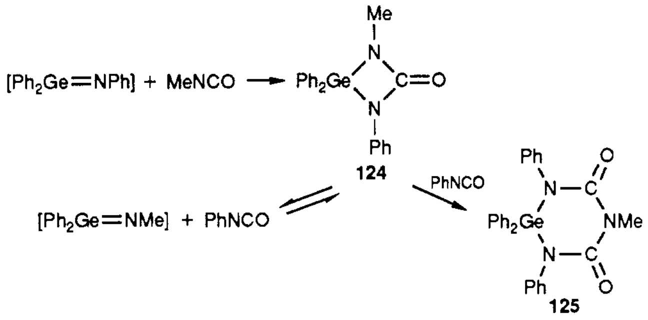
The germadihydrotriazoles **122** decompose partly at or above room temperature in a first-order reaction either by isomerization into diazomethane derivative **123** (route a) or by [2 + 3] cycloreversion into $(Me_3Si)_2C{=}N{=}N$ and germanimines $Me_2Ge{=}NR$ (route b). These germanimines are formed as short-lived intermediates, which dimerize^{5,25} (Scheme 23).

Reactions of germanimines $Me_2Ge{=}NR$ with its precursor **122** (for R = $SiMe_3$)^{25b,143} (Scheme 24) and

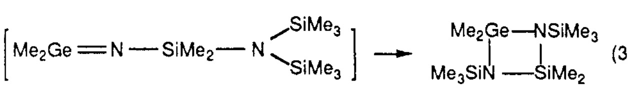
SCHEME 25



SCHEME 26



an intramolecular migration process (R = $SiMe_2N(SiMe_3)_2$, $SiPh_3$)[25b,143] (eq 35) are also observed.

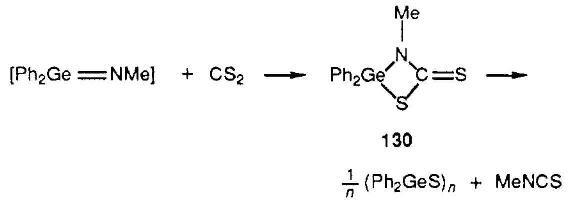
 (35)

Germanimines are characterized in the form of polygermazanes by insertion into the germanium–nitrogen bond of germylazetidine and dimethyl(triethylgermyl)amine and by insertion into a tetrahydrofuran ring and formation of a seven-membered heterocycle as well as pseudo-Wittig reaction with benzaldehyde and formation of unstable germaoxaazetidine[6–8,135–137] (Scheme 25).

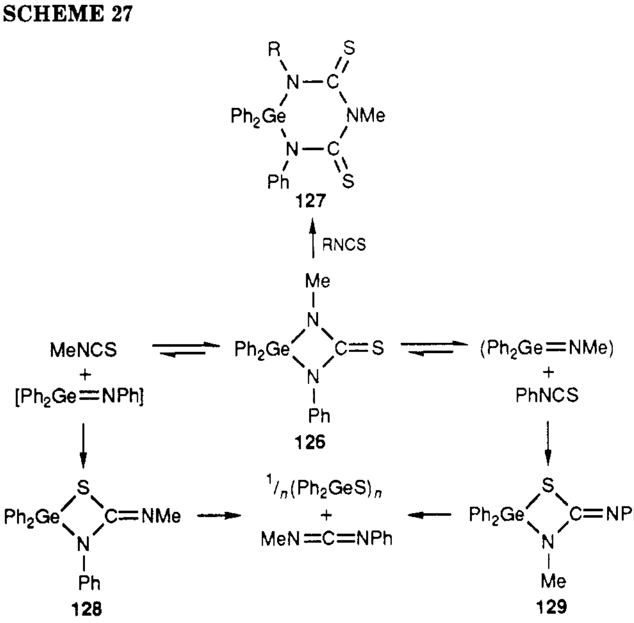
The 1,2-cycloadditions of germanimines with phenyl or methyl isocyanates produce unstable germaoxodiazetidine **124** which leads to 2-germa-4,6-dioxo-1,3,5-perhydrotriazine **125**[140] (Scheme 26).

In the case of isothiocyanates, the formation of adducts from C=N and C=S addition is observed. Addition across the C=N bonds leads to 2-germa-4-thioxo-1,3-diazetidine **126** and 2-germa-4,6-thioxo-1,3,5-perhydrotriazine **127**. Addition across the C=S bond leads to unstable 2-germa-4-(methylimino)-1,3-thiazetidine **128** and 2-germa-4-(phenylimino)-1,3-thiazetidine **129**, which decompose to diphenylgermanium sulfide dimer and trimer and carbodiimide[140] (Scheme 27).

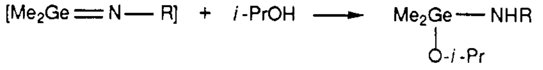
N-Methyldiphenylgermanimine [from $Ph_2Ge(NMe_2)_2$ + PhNCO] adds to CS_2 with formation of unstable 2-germa-4-thioxo-1,3-thiaazetidine **130**[140] (eq 36).

 (36)

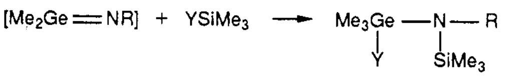
SCHEME 27



Germanimines $Me_2Ge{=}NR$ (R = $SiMe_3$, $SiMe_2$-*t*-Bu, SiMe-*t*-Bu_2, $SiMe_2N(SiMe_3)_2$, $GeMe_2N(SiMe_3)_2$) generated as reactive intermediates by thermal [2 + 3] cycloreversion from cycloadducts of $Me_2Ge{=}C(SiMe_3)_2$ or $Me_2Ge{=}NR$ with silyl azides RN_3 combine with amine $EtNMe_2$ to afford the adducts[50] $EtMe_2N{\rightarrow}Ge(Me_2){=}NR$. These germanimines undergo addition reactions with *i*-PrOH, Me_3SiN_3, and $Ph_2CNSiMe_3$ (eq 37 and 38). Germanimines give also [2 + 2] cycloadditions with themselves by dimerization (eq 39) and with $Ph_2C{=}O$ (eq 40). However, ene reactions are observed with $CH_2{=}CHCH_2H$ and $O{=}CMeCH_2H$ (eq 41). Reactions with azidoalkanes or -silanes $R'N_3$ (R′ = *t*-Bu, $SiMe_n$-*t*-Bu_{3-n}, $SiPh_3$, $SiMe_2N(SiMe_3)_2$) yield germatetrazoles **131**[50,143] (eq 42). The formation of insertion products of $Me_2Ge{=}NR$ into the R′N bond of the azides $N{=}N{=}NGe(Me_2)NRR'$ is also noted.

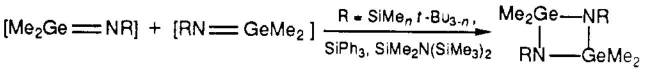
 (37)

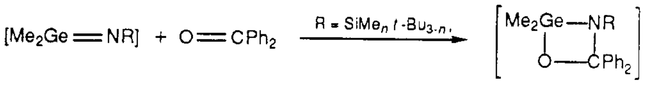
$$[\mathrm{Me_2Ge{=}N{-}R}] + i\text{-PrOH} \longrightarrow \mathrm{Me_2}\underset{\mathrm{O}\text{-}i\text{-}\mathrm{Pr}}{\mathrm{Ge}}\mathrm{{-}NHR} \quad (37)$$

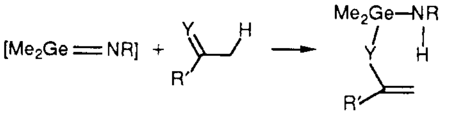
 (38)

$$[\mathrm{Me_2Ge{=}NR}] + \mathrm{YSiMe_3} \longrightarrow \mathrm{Me_3}\underset{\mathrm{Y}}{\mathrm{Ge}}{-}\underset{\mathrm{SiMe_3}}{\mathrm{N}}{-}\mathrm{R} \quad (38)$$

Y = N_3, Ph_2CN

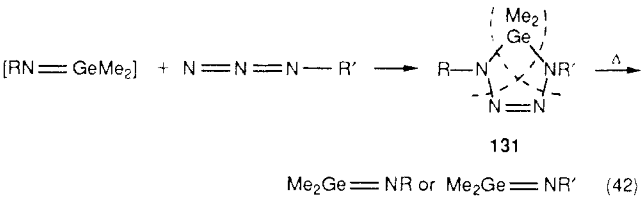
 (39)

 (40)

 (41)

Y = CH_2, O

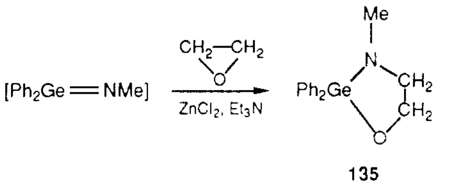
The germadihydrotetrazoles **131** decompose at elevated temperatures in a first-order reaction, reversing their formation by [2 + 3] cycloreversion into azides



(42)

$R'N_3$ or RN_3 and germanimines $Me_2Ge{=}NR'$ or $Me_2Ge{=}NR$. The germanimines are formed only as short-lived intermediates. Consequently, azides operate as stores for germanimines[143] (eq 42).

The [2 + 3] cycloadditions of germanimines $RR'Ge{=}NR''$ (R = Ph; R' = Ph, Cl; R'' = Me, Ph, *t*-Bu) with nitrones **132** (diphenyl- or phenyl-*tert*-butylnitrone) as well as their insertion reactions on oxaziridines **133** lead to germanones ($RR'Ge{=}O$), imines $PhCH{=}NR''$, and nitrenes, probably via transient 2-germa-1-oxa-3,5-diazolidines **134**. The imines formed contain the NR'' group of the initial germanimines[140,141] (Scheme 28). Similar reactions are observed with dichloro-*N*-methylgermanimine (from ring opening of chlorocyclotrigermazanes catalyzed by Lewis bases (HMPA) or Lewis acids ($ZnCl_2$, $M(CO)_6$, $M(CO)_5{\cdot}THF$ (M = Cr, W)).[142] Germanimines obtained from catalytic depolymerization of cyclodigermazane by $ZnCl_2$ or Et_3N insert into ethylene oxide with formation of 2-germa-1,3-oxazolidine **135**[140] (eq 43). Reactions of diazo compounds R'_2CN_2 (R'_2C = fluorenylidene or Ph_2) with germene $Mes_2Ge{=}CR_2$ (**35**) lead to cyclodigermazanes **48** and **51**, probably via transient germanimines **52**, with evolution of carbene CR_2 and formation of R_2CH_2[65] (cf. eq 16–18).



(43)

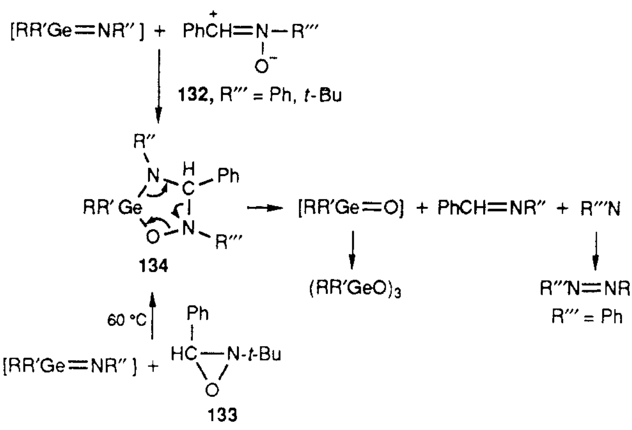
The transient diphenyl-*N*-mesitylgermanimine ($Ph_2Ge{=}NMes$) (from dehydrohalogenation of $Ph_2ClGeNHMes$ by DBU) gives unstable 1,4 adducts **136** and 1,2 adducts **137** with di-*tert*-butyl-3,5-*o*-quinone[223] (Scheme 29).

(2) Stable Germanimines

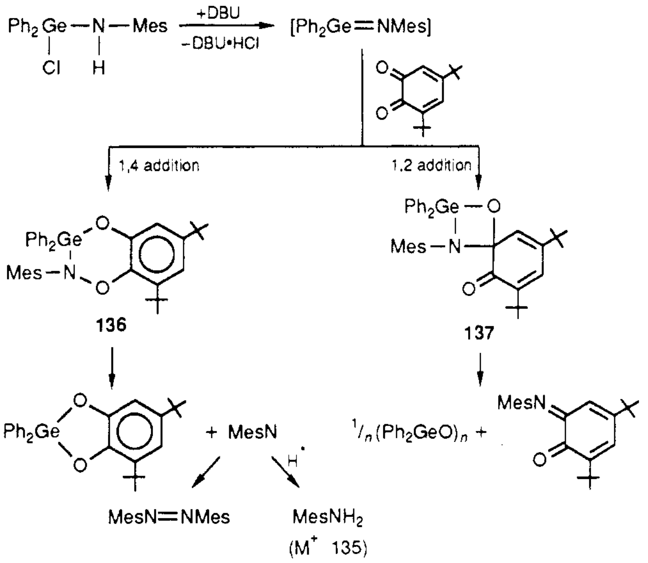
The electron-rich germylene $Ge[N(SiMe_3)_2]_2$ reacts with the diazo compound $N_2C(COOMe)_2$ to give germyleneazines $[(Me_3Si)_2N]_2Ge{=}N{-}N{=}C(COOMe)_2$ (**138**).[144-146] Two forms of the stable germyleneazine have been characterized in solution by ^1H and ^{13}C NMR spectroscopy. MNDO calculations on the simpler analogue $[(H_2Si)_2N]_2GeNNC(COOMe)_2$ indicate that the two forms have planar transoid **138a** and cisoid **138b** GeNNC groups, respectively, with the cisoid isomer as the more stable (Scheme 30). The calculations also indicate that charge-controlled additions of electrophiles will occur at nitrogen adjacent to germanium while all nucleophilic additions will occur at Ge.[144,145]

Some adducts of $[(Me_3Si)_2N]_2Ge{=}N{-}N{=}C(COOMe)_2$ (**138**) with weak acids HX are described. In all cases 1,2-addition of HX occurs across the Ge–N bond to yield $[(Me_3Si)_2N]_2Ge(X)[NHN{=}C(COOMe)_2]$ (Scheme 31). The reaction with water is

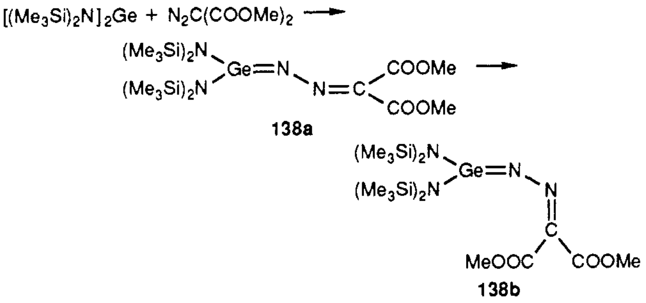
SCHEME 28



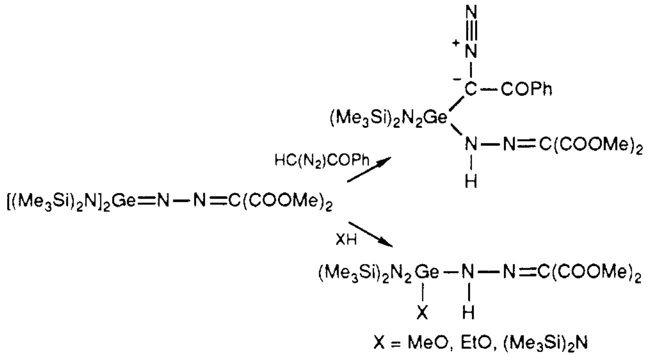
SCHEME 29



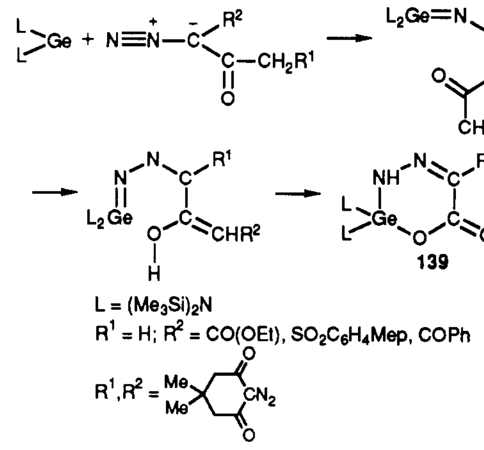
SCHEME 30



SCHEME 31



SCHEME 32



139

L = $(Me_3Si)_2N$

R^1 = H; R^2 = CO(OEt), $SO_2C_6H_4Mep$, COPh

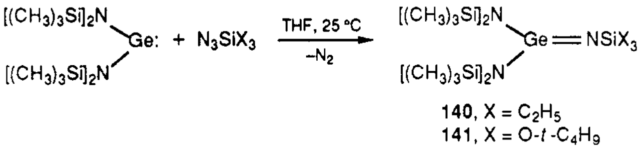
more complex; when at least 2 molar equiv of water is used, the germyleneazine undergoes complete cleavage of the unique Ge–N bond to give the germanediol $(HO)_2Ge[N(SiMe_3)_2]_2$ together with the hydrazone $H_2NN{=}C(COOMe)_2$. When only 1 molar equiv of water was added to $[(Me_3Si)_2N]_2GeNNC(COOMe)_2$, the products included not only $Ge(OH)_2[N(SiMe_3)_2]_2$ and $H_2N-N{=}C(COOMe)_2$ but also the very labile $[(Me_3Si)_2N]_2Ge(OH)[NH-N{=}C(COOMe)_2]$, which decomposes to $^1/_n[GeO[N(SiMe_3)_2]_2]_n$ and $H_2N{=}N-C(COOMe)_2$. The same germylene $Ge[N(SiMe_3)_2]_2$ reacts with other diazo compounds $R^1CH_2COC(N_2)R^2$ that contain an enolizable function to yield the heterocycles $[(Me_3Si)_2N]_2GeNH-N{=}C(R^2)C({=}CHR^1)O$ (**139**)[146] (Scheme 32). The crystal and molecular structure of one of these compounds **139** (R^1 = H, R^2 = COOEt) has been described.[147]

The weakly acidic diazo compounds ethyl diazoacetate and diazoacetophenone yield bis adducts $[(Me_3Si)_2N]_2Ge[C(N_2)COR][NH-N{=}CHCOR]$ (R = OEt or Ph).[146]

All the reactions of germylene with these diazo compounds can be rationalized in terms of the initial formation of a germyleneazine $[(Me_3Si)_2N]_2Ge{=}N-N{=}C(X)Y$ formed by initial addition of the terminal nitrogen of the diazo group to the germylene $Ge[N(SiMe_3)_2]_2$. The adduct, containing a Ge=N bond, can be trapped either intramolecularly in the presence of enolizable groups or by addition of weakly protic species. The characterization of the germyleneazine $[(Me_3Si)_2N]_2Ge{=}N-N{=}C(COOMe)_2$ (**138**) represents the first system containing three-coordinate germanium forming a formal double bond, which does not rely on the presence of sterically bulky substituents at both ends of the double bond to confer kinetic persistence.[144-146]

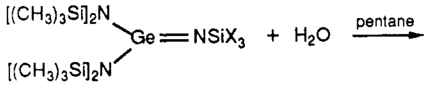
Reaction of germylene $Ge[N(SiMe_3)_2]$ with tosyl azide follows a different course from the reaction involving diazo compounds; nitrogen is lost and the product is a polygermazane $[(Me_3Si)_2N]_2GeNSO_2C_6H_4Me\text{-}p]_n$. The product probably arises via the formation of transitory germanimine $[(Me_3Si)_2N]_2Ge{=}NSO_2C_6H_4Me\text{-}p$.[145]

Two stable germanimines **140** and **141** have recently been characterized from the action of bis[bis(trimethylsilyl)amino]germylene on triethylsilyl azide or tri-*tert*-butoxysilyl azide[148] (eq 44). The germanimines are characterized by MS, ^1H NMR, and ^{29}Si NMR. Germanimines **140** and **141** are white solids that quickly react with water to form triamino hydroxygermanes **142** (eq 45).



140, X = C_2H_5
141, X = O-*t*-C_4H_9

(44)



$$[[(CH_3)_3Si]_2N]_2Ge(OH)NHSiX_3 \quad (45)$$

142a, X = C_2H_5
b, X = O-*t*-C_4H_9

Methanol reacts only with **141** to give triamino methoxygermane **143** (eq 46).

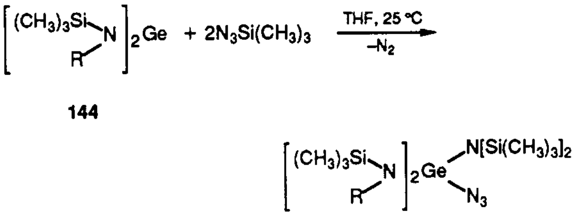
$$[[(CH_3)_3Si]_2N]_2Ge{=}NSi(O\text{-}t\text{-}C_4H_9)_3 + CH_3OH \longrightarrow$$

141

$$[[(CH_3)_3Si]_2N]_2Ge(OCH_3)NHSi(O\text{-}t\text{-}C_4H_9)_3 \quad (46)$$

143

The reactions of diazagermylenes $[(CH_3)_3Si(R)N]_2Ge$ **144** (R = $(CH_3)_3Si$, 2,6-$(CH_3)_2C_6H_3$, 2,4,6-$(CH_3)_3C_6H_2$) with trimethylsilyl azide lead to azido germanium derivatives **145** (eq 47), probably via transitory formation of germanimines followed by addition of trimethylsilyl azide on the Ge=N double bond.

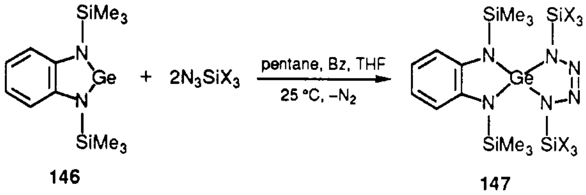


144

145

(47)

Reaction of germa(II)indane **146** with N_3SiX_3 (X = CH_3, C_2H_5) leads to the germatetragermoles **147** (eq 48), probably by preliminary formation of an unstable germanimine followed by [2 + 3] cycloaddition of triorganosilyl azide.

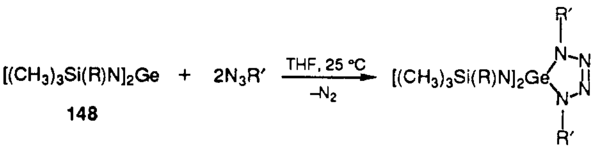


146

147

(48)

By the same route the sterically hindered germylenes $[(CH_3)_3Si(R)N]_2Ge$ **148** react with phenyl and benzyl azides to give the corresponding germatetrazole **149** (eq 49).



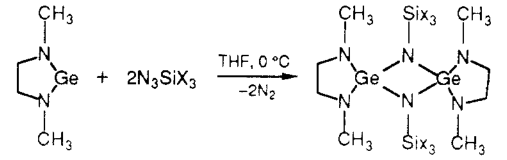
148

(49)

149

R = $(CH_3)_3Si$, 2, 6-$(CH_3)_2C_6H_3$, 2, 4, 6-$(CH_3)_3C_6H_2$
R′ = C_6H_5, $CH_2C_6H_5$

The reactions of less hindered diazagermylene **150** with N_3SiX_3 (X = CH_3, O-*t*-C_4H_9) lead to hexaazadigermadispirododecanes **151**, the dimer of the transient germanimine[148] (eq 50).



151

X = CH_3, O-*t*-C_4H_9

A new stable germanimine, *N*-(trifluoromethyl)germanimine $CF_3N{=}GeH_2$ (**152**), was recently synthesized by reaction of CF_3NO and GeH_4 and characterized by IR and electron impact mass spectrometry[149] (eq 51).

$$CF_3NO + GeH_4 \longrightarrow \underset{\mathbf{152}}{CF_3N{=}GeH_2} + H_2O \quad (51)$$

N-(Trifluoromethyl)germanimine (**152**) was isolated at −96 °C in a trap-to-trap fractionation under high vacuum as a white solid in 25% yield. At room temperature the germanimine **152** became a colorless gas. On standing in an evacuated ampule for 2 days at room temperature, the germanimine **152** underwent polymerization.

The presence of the Ge=N double bond in this germanimine was chemically confirmed by its reaction with hydrogen iodide, which gave the product CF_3NHGeH_2I in 33% yield.

The presence of the GeH_2 moiety in *N*-(trifluoromethyl)germanimine (**152**) was confirmed by its reaction with bis(trifluoromethyl)nitroxyl, which is a powerful hydrogen abstractor and a radical scavenger (eqs 52 and 53). The new [bis(trifluoromethyl)nitroxy]germanimines **153** and **154** were isolated at −70 °C as white solids. They are stable at room temperature. Cleavage of the Ge–O bonds of both the [bis(trifluoromethyl)nitroxy]germanimines **153** and **154** by hydrogen chloride afforded the corresponding chloro derivatives **155** and **156** in 53% and 57% yields, respectively (eqs 54 and 55). Compounds **155** and **156** are stable at −20 °C. On standing for 1 day at room temperature in evacuated ampules, both **155** and **156** deposited some nonvolatile solids.

$$CF_3N{=}GeH_2 + 2(CF_3)_2NO \longrightarrow \underset{\mathbf{153}}{CF_3N{=}Ge(H)ON(CF_3)_2} + (CF_3)_2NOH \quad (52)$$

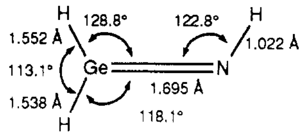
$$CF_3N{=}GeH_2 + 4(CF_3)_2NO \longrightarrow \underset{\mathbf{154}}{CF_3N{=}Ge[ON(CF_3)_2]_2} + 2(CF_3)_2NOH \quad (53)$$

$$CF_3N{=}Ge(H)ON(CF_3)_2 + HCl \longrightarrow \underset{\mathbf{155}}{CF_3N{=}GeHCl} + CF_3NOH \quad (54)$$

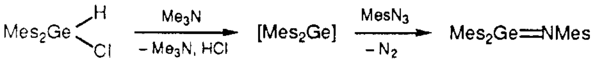
$$CF_3N{=}Ge(ON(CF_3)_2)_2 + 2HCl \longrightarrow \underset{\mathbf{156}}{CF_3N{=}GeCl_2} + 2CF_3NOH \quad (55)$$

The presence of the Ge=N double bond in the new germanimines **153**, **154**, **155**, and **156** was indicated by their IR spectra, which gave absorption peaks located at 1028, 1070, 1057, and 1076 cm^{-1},[149] respectively, which are slightly higher than the band at 970 cm^{-1} reported for the $F_2Ge{=}NPh$ double bond.[6] The stability of these nonhindered germanimines described in this paper[149] is, however, rather surprising.

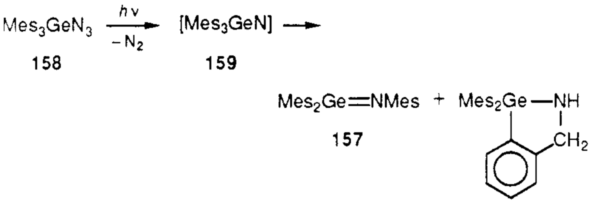
SCHEME 33



Trimesitylgermanimine ($Mes_2Ge{=}NMes$ (**157**)) was obtained by reaction between dimesitylgermylene and mesityl azide (eq 56) and also by photolysis of trimesitylgermyl azide (**158**). Transitory formation of (trimesitylgermyl)nitrene (**159**) and Curtius-like rearrangement are postulated in this rearrangement.[150] The cyclic isomer **160** is also formed by insertion of germylnitrene into the C–H bond of the mesityl group (eq 57).



$$Mes_2Ge\begin{smallmatrix}H\\Cl\end{smallmatrix} \xrightarrow[-Me_3N,\ HCl]{Me_3N} [Mes_2Ge] \xrightarrow[-N_2]{MesN_3} \underset{\mathbf{157}}{Mes_2Ge{=}NMes} \quad (56)$$



158 **159** **157** **160**

Hydrolysis by HCl carried out at the end of the photolysis reaction leads to Mes_2GeCl_2, thus confirming the Curtius-like rearrangement.[150]

Trimesitylgermanimine (**157**) has been characterized by pseudo-Wittig reaction with benzaldehyde and formation of $PhCH{=}NMes$ and $(Mes_2GeO)_2$.[150] Recently, Ando et al.[228] have characterized **157** by irradiation of Mes_3GeN_3 in a 3-methylpentane matrix at 77 K. The formation of azagermacyclopentene **160** is also observed (50% yield). $Mes_2Ge{=}NMes$ (**157**) is intensely yellow with absorption maxima at 309 and 459 nm. This assignment agrees with that of West et al. for the analogous silanimine $Mes_2Si{=}NMes$, which has absorption maxima at 296 and 444 nm.[229,230]

In the presence of ethanol, in addition to a 50% yield of **160**, diethoxydimesitylgermane (**161**) and 2,4,6-trimethylaniline (**162**) were obtained in 14% and 11% yields, respectively (eq 57a).

$$\underset{\mathbf{157}}{Mes_2Ge{=}NMes} + 2EtOH \longrightarrow \underset{\mathbf{161}}{Mes_2Ge(OEt)_2} + \underset{\mathbf{162}}{MesNH_2} \quad (57a)$$

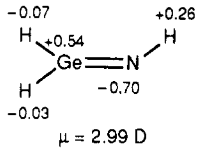
(3) Theoretical Studies

Germanimine ($H_2Ge{=}NH$) is predicted to be a planar molecule.[26] Its optimized geometry at the SCF level is shown in Scheme 33.

The Ge=N bond length (1.695 Å) is shorter than a normal Ge–N σ bond (1.83–1.87 Å[148,151]). The length, force constant, and absorption frequency of the Ge=N (noncoupled) bond at the CI level are found to be $\delta_{Ge=N}$ = 1.727 Å, $K_{Ge=N}$ = 5.37 mdyn/Å, and $\nu_{Ge=N}$ = 854 cm^{-1}.

The germylene isomer $HGeNH_2$ is calculated to be more stable than the doubly bonded form $H_2Ge{=}NH$.

SCHEME 34



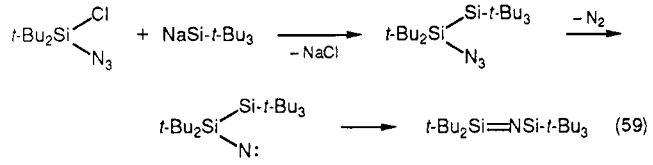
The energy difference between $HGeNH_2$ and $H_2Ge{=}NH$ is 32 kcal/mol. The relative stabilization of aminogermylene is enhanced by delocalization of a π lone pair in the vacant germanium $p\pi$ orbital. The charge distribution and dipole moment of the germanimine is shown in Scheme 34. The theoretical analysis and experimental studies of the flash pyrolysis of trimethylgermyl azide **163** combined with calculations of the ionization potentials of the rearrangement products have led to the conclusion of the formation of germaisonitrile **164** as the thermolysis product[152] (eq 58).

$$\underset{163}{(CH_3)_3GeN_3} \xrightarrow[1100\ K,\ 10^{-2}\ mbar]{} \underset{164}{[Ge{\equiv}NH]} + N_2 \qquad (58)$$

(4) Stable Silanimines

The stable silanimine $t\text{-}Bu_2Si{=}N\text{-}t\text{-}Bu$ has been prepared in quantitative yield from the reaction between azidodi-*tert*-butylchlorosilanes and (tri-*tert*-butylsilyl)sodium in dibutyl ether at −78 °C.

The mechanism of this reaction is not well understood. It seems that the silanimine could be formed after a sequence of substitution reactions, formation of silylnitrene, and Curtius-like rearrangement (eq 59).



$t\text{-}Bu_2Si{=}Ni\text{-}t\text{-}Bu$ has been structurally characterized by X-ray analysis (Si=N = 1.568 Å, Si–N–Si = 177 (8)°).[224]

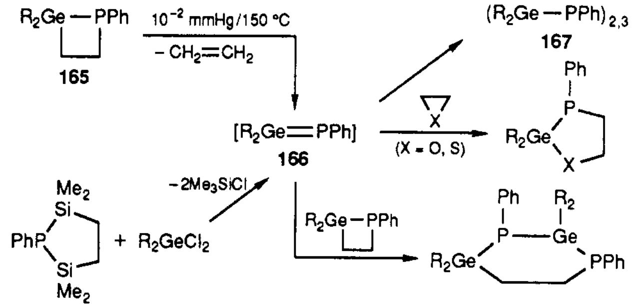
The same silanimine can be obtained by thermal elimination of LiCl from $(t\text{-}Bu)_2ClSi\text{-}NLi\text{-}Si(t\text{-}Bu)_3$.[225] A free silanimine, diisopropyl[(2,4,6-tri-*tert*-butylphenyl)imino]silane, has been isolated by elimination of LiCl from chlorodiisopropyl[*N*-lithio-*N*-(2,4,6-tri-*tert*-butylphenyl)amino]silane heated in a vacuum at 0.01 mbar. The silanimine sublimes at 80 °C. It is an orange crystalline solid which melts without decomposition to give a deep red liquid.[226]

V. Ge=P Species: Germaphosphenes

(1) Transient Germaphosphenes

Until recently, germaphosphenes RR′Ge=PR″ were postulated only as reactive intermediates and characterized by trapping reactions. These highly reactive and short-lived species were obtained by two routes: thermal decomposition of the four-membered heterocycles 2-germaphosphetanes **165**[153] and dechlorosilylation between dialkyldichlorogermanes and disilylphosphines.[154] The transient germaphosphenes **166** were clearly characterized by formation of dimeric or trimeric cyclic germylphosphine **167** and by insertion and ring-expansion reactions with strained three- or four-membered heterocycles (Scheme 35).

SCHEME 35

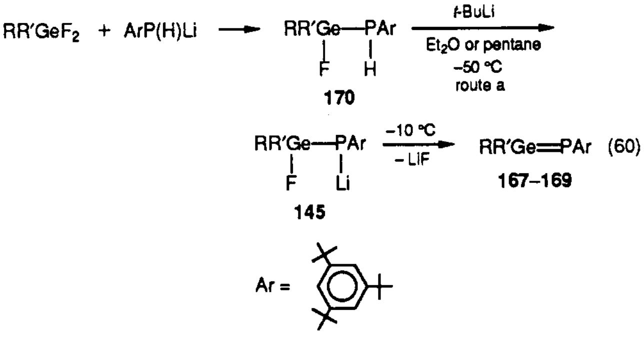


In the case of silicon and tin, sila- and stannaphosphenes RR′M=PR″ (M = Si,[155] Sn[156]) could also until recently only be obtained and characterized by similar procedures.

(2) Stable Germaphosphenes

(a) Synthesis

Owing to substituents having strong steric hindrance and electronic effects, three stable germaphosphenes—**167**,[157] **168**,[158] and **169**[158]—have recently been obtained. The best route to **167–169**, which is nearly quantitative, is the dehydrofluorination of the corresponding fluorogermylphosphines **170** by *tert*-butyllithium at low temperature (eq 60).



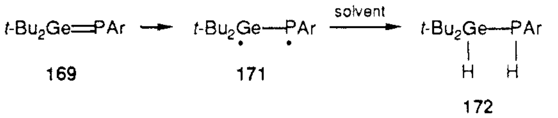
RR′ = Mes₂ (**167**),[157] Mes, *t*-Bu (**168**),[158] *t*-Bu₂ (**169**)[158]

In the case of **169**, the best yield (75%) is obtained by using pentane as solvent for the dehydrofluorination. With diethyl ether, the lithiophosphine is quite stable[158] and leads after 24 h at 25 °C to the expected germaphosphene only in poor yield. The major product is the germylphosphine $t\text{-}Bu_2Ge(H)P(H)Ar$, probably formed via biradical **171**.

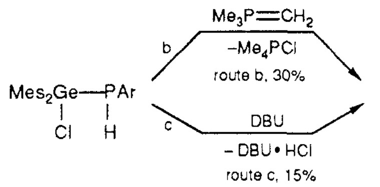
In solution in pentane **169** gives after 1 week at room temperature the germylphosphine **172**; this transformation is much more rapid in diethyl ether. So it seems that, contrary to **167**, the germaphosphene **169** substituted on germanium by two alkyl groups has some radical character (eq 61).

Two other routes, routes b and c, to germaphosphenes starting from chlorogermylphosphines have also been used but lead to **167** only in poor yield[157] (eq 62).

In the case of **168**, starting from a 60/40 mixture of the diastereoisomers **173**, a sole isomer **168a** is obtained after reaction at low temperature.[158] This phenomenon is explained by the preferential reaction of one diastereoisomer of **173** and by a rapid thermodynamic equilibrium between the two diastereoisomers of **173**, probably due to the configurational instability of

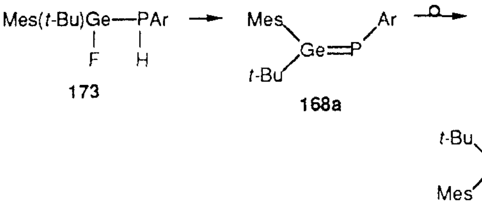


(61)



(62)

asymmetric fluorogermanes.[159] After 5 h at room temperature the ratio **168a**/**168b** becomes nearly 0/100 (eq 63).



(63)

The structure of **168b** has been proved by X-ray analysis (see section V.2.b).

The cis–trans isomerization barrier (22.3 kcal/mol) has been determined by NMR. A similar value was experimentally obtained for diphosphene ArP=PAr (Ar = 2,4,6-tri-*tert*-butylphenyl); but in the case of germene ($H_2Ge{=}CH_2$), the calculated isomerization barrier is much higher (31 kcal/mol)[59] (see section II).

Note, however, the large discrepancy between the experimental value for ArP=PAr (22.3 kcal/mol)[160] and the theoretical value for HP=PH (34 kcal/mol);[161] this is probably due to the very important steric and electronic effects of the very bulky Ar group. Values higher than the 22.3 kcal/mol found for germaphosphene **168b**[158] are also calculated for silaphosphene ($H_2Si{=}PH$)[161] and for phosphene ($H_2C{=}PH$).[161,162]

(b) Physicochemical Studies

The yellow-orange crystals of **167** and **168b** are air and moisture sensitive but very thermally stable (until 150 °C); they can be stored without change for months in an inert atmosphere.

Germaphosphenes **167**, **168**, and **169** are thermochromic: they are yellow at −80 °C, orange at room temperature, and orange-red at +80 °C. Such a reversible phenomenon has previously been noted in other doubly bonded species like disilenes[2b] or diphosphenes.[9] The vibrational population of the electronic ground state changes drastically from low to room temperature ($\nu_{Ge=P} = 500\ cm^{-1} \sim 1.4$ kcal/mol), and from this reorganization a red shift of the electronic absorption is expected according to the Franck–Condon principle.[158]

A rather important temperature dependence of 12–14 ppm has been observed for the ^{31}P chemical shift of germaphosphenes (see Table 7).[158] Increasing the temperature causes a low-field shift in connection with the red shift of the electronic absorption: an analogous connection between electronic absorption and ^{119}Sn chemical shifts has been observed in the series $Ph_3Sn(Sn\text{-}t\text{-}Bu_2)_nSnPh_3$ ($n = 1$–4).[163]

TABLE 7. Variation of $\delta(^{31}P)$ Chemical Shifts with Temperature (ppm)

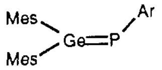
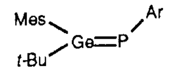
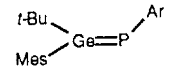
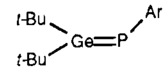
	^{31}P NMR		
germaphosphene	−80 °C	+20 °C	+80 °C
	+164.8	+173.6	+178.2
		+169.2	
	+149.1	+157.4	+161.0
	+148.5	+156.6	+159.8

TABLE 8. Important Bond Lengths (Å) and Angles (Deg) with Esd's in Parentheses and Raman Emission for 167 and 168b

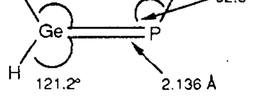
	$Mes_2Ge{=}PAr$ (**167**)	$Mes(t\text{-}Bu)Ge{=}PAr$ (**168b**)
bond lengths		
Ge=P	2.138 (3)	2.144 (3)
P–Ar	1.86 (1)	1.86 (1)
Ge–C (cis to lone pair)	1.94 (1)	1.97 (1)
Ge–C (trans to lone pair)	1.96 (1)	2.01 (1)
bond angles		
Ar–P–Ge	107.5 (3)	102.6 (3)
P–Ge–C (cis to lone pair)	111.8 (3)	114.4 (3)
P–Ge–C (trans to lone pair)	135.2 (4)	134.7 (4)
C(cis)–Ge–C(trans)	112.9 (4)	110.9 (5)
Raman (cm^{-1})	503	501.5

The ^{31}P chemical shifts (148.5–178.2) (see Table 7) are characteristic of dicoordinated phosphorus. As in the case of stable germenes, germanimines, and digermenes, no ^{73}Ge NMR signal could be detected. ^{73}Ge NMR gives good results only in the case of relatively symmetrical molecules. Compounds **167** and **168b** have strong Raman emission at 503 and 501.5 cm^{-1} (see Table 8).[158] A good correlation is observed with previous calculations using pseudopotentials: the value obtained by Barthelat with configuration interaction is 481 cm^{-1}.[167]

The structures of **167** and **168b** have been determined by X-ray crystallography[158,166] (Figures 5 and 6). The germanium–phosphorus double-bond length (2.138 and 2.144 Å; see Table 8) is substantially shorter than the standard germanium–phosphorus single bond (2.33–2.35 Å).[96,168–173] This shortening of about 8.5% (about the same as that in other main-group doubly bonded species) and the essentially planar double-bond geometry (the sum of the angles on germanium is 360° and the five atoms $C_2Ge{=}PC$ are in the same plane) support the existence of a true double bond.

When the germanium is substituted by two different groups (mesityl and *tert*-butyl), the most stable isomer has the *tert*-butyl group cis to the tri-*tert*-butylphenyl group.[158] Such an arrangement may seem surprising, since *tert*-butyl is considered to be bulkier than mesityl;[174] however, it is the sole possibility allowing free rotation of all groups, which is not possible when mesityl and tri-*tert*-butylphenyl are cis.

A good correlation between calculations and experiment was observed for bond lengths and angles in Ge=P.[167]



(64)

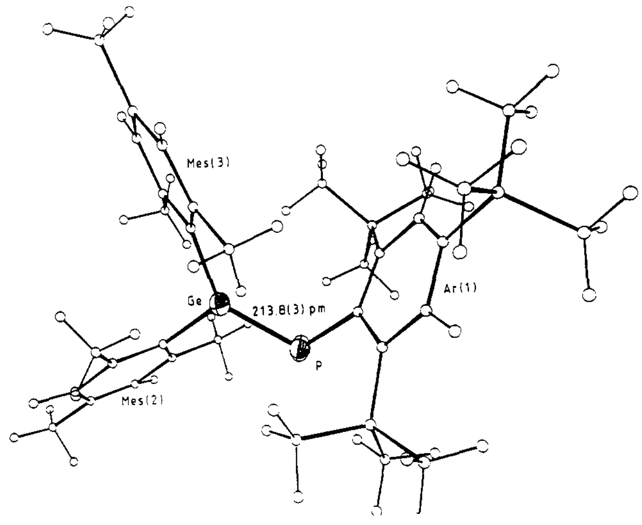


Figure 5. ORTEP view of **167** (reprinted from *Organometallics* **1988**, *7*, 1010; copyright 1988 American Chemical Society).

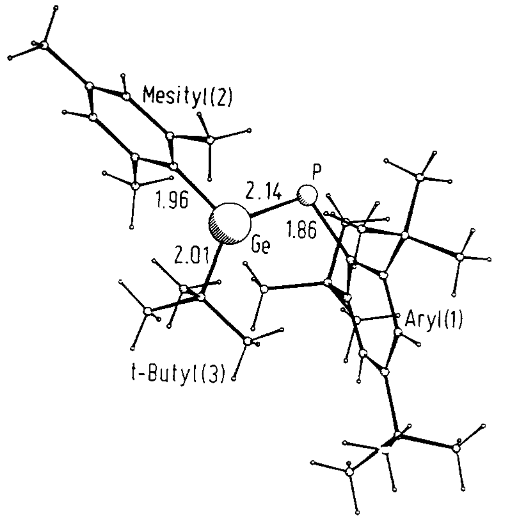
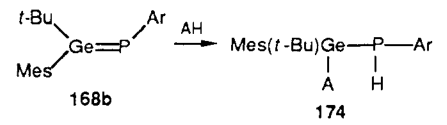


Figure 6. ORTEP view of **168b** (reprinted from *New J. Chem.* **1989**, *13*, 389; copyright 1989 CDR—Centrale des Revues).

(c) Chemical Reactivity of 167 and 168b

The double-bond character of the germanium–phosphorus connection, as shown by X-ray data, was also supported by the study of the chemical reactivity. Only a behavior of a doubly bonded compound was observed and never a behavior of germylene R_2Ge: and phosphinidene ArP, as if the germanium–phosphorus connection was very weak.

Germaphosphene **168b** reacts regiospecifically with protic reagents such as fluorhydric acid or water;[158] germylphosphines **174** are obtained in a nearly quantitative yield. Immediately after reaction, ^{31}P NMR shows a mixture of two diastereoisomers in the ratio 60/40, due to a rapid thermodynamic equilibrium (eq 65).



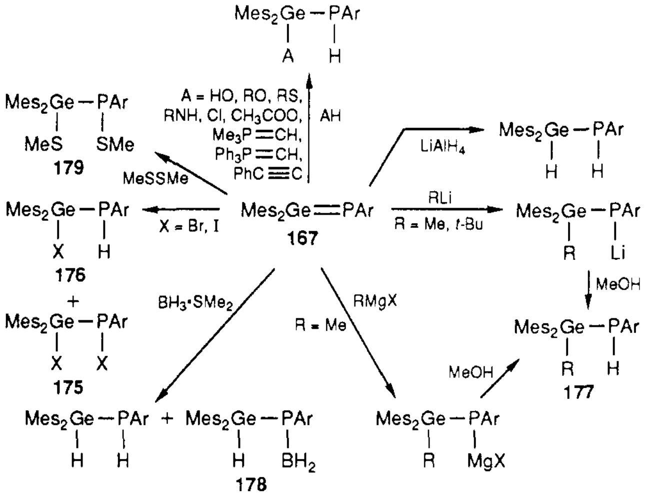
$$(t\text{-Bu})(\text{Mes})\text{Ge}{=}\text{PAr} \xrightarrow{\text{AH}} \text{Mes}(t\text{-Bu})\underset{\text{A}}{\text{Ge}}\text{—}\underset{\text{H}}{\text{P}}\text{—Ar} \qquad (65)$$

168b **174**

A = F,HO

Germaphosphene **167** is very reactive toward compounds having active hydrogens such as water,[157,185] alcohols,[157,185] thiols,[175,185] amines,[175,185] mineral and organic acids,[157,175,185] phosphorus ylides,[157,185] and acetylenic compounds[175,185] (Scheme 36). These additions are highly regiospecific, producing only secondary phosphines. The regiochemistry is determined particularly by polar effects arising from the fact that germanium (electronegativity 2.0[51,52]) is more electropositive than phosphorus (2.1[51,52]). The indicated germanium-phosphorus bond polarity $Ge^{\delta+}{=}P^{\delta-}$ is in good agreement with calculations.[167]

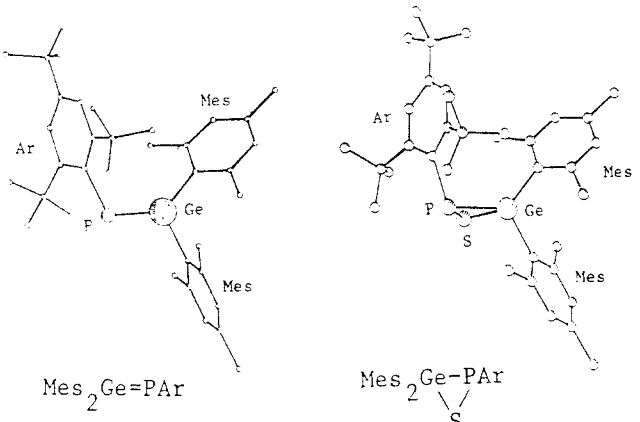
SCHEME 36



Bromine and iodine react with **167** to produce the expected adduct **175** and, surprisingly, the halogermylphosphine **176** as a major product.[175,185] The formation of **175** and **176** probably involves two competitive mechanisms: an electrophilic addition on the double bond and a radical process with an intermediate $Mes_2Ge(X)P^{\bullet}Ar$ abstracting $X^{\bullet}$ (formation of **175**) and $H^{\bullet}$ (formation of **176**) from the solvent. Nucleophiles such as lithio compounds or Grignard reagents add easily to the double bond, affording deep red solutions characteristic of the presence of the phosphorus anions.[175,185] Quenching with methanol gives the new germylphosphines **177**. Reduction of the germanium–phosphorus double bond is observed with lithium aluminum hydride and borane, together with the adduct **178** in this last case[175,185] (Scheme 36). Similar additions of lithio compounds have been observed on diphosphenes.[176,177]

Germaphosphene **167** reacts with dimethyl disulfide, probably by a radical process, leading to **179** (Scheme 36). Even with a large excess of dimethyl disulfide, cleavage of the germanium–phosphorus single bond has not been observed.[175,185] The same phenomenon occurs with electrophiles and nucleophiles, which react only with the double bond. The fact that the Ge–P single bond, which is usually cleaved by lithio compounds,[178] Grignard reagents,[179] hydrides,[180] and dimethyl disulfide,[181] is unaffected is probably due to the very large steric hindrance of the mesityl and tri-*tert*-butylphenyl groups.

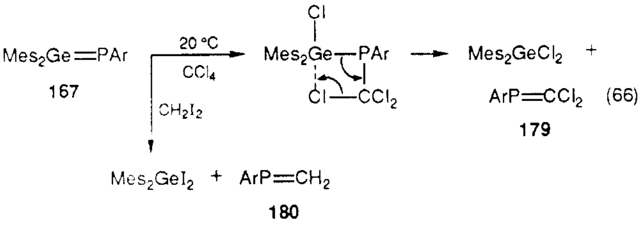
Reactions of germaphosphene **167** with halogenated compounds such as carbon tetrachloride or diiodomethane[175,185] are particularly interesting because they lead to phosphaalkenes **179** and **180**, unsaturated compounds of phosphorus with a carbon–phosphorus double bond. The first step of this reaction is probably the addition of carbon tetrachloride (or diiodomethane) to the germanium–phosphorus double bond followed by a β elimination initiated by the affinity of chlorine for germanium[186] (eq 66). Phosphaalkenes $ArP{=}CCl_2$[183]



167 **181a**

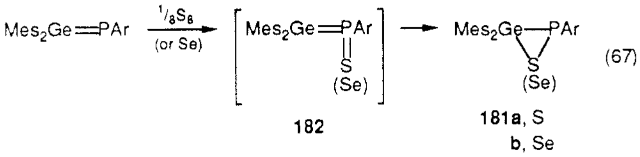
Figure 7. ORTEP and PLUTO views of respectively **167** and **181a** (reprinted from *Organometallics* **1988**, *7*, 1010 (**167**), and *Organometallics* **1988**, *7*, 1545 (**181a**); copyright 1988 American Chemical Society).

and $ArP{=}CH_2$[184] have been prepared through other routes by Appel and Issleib, respectively.



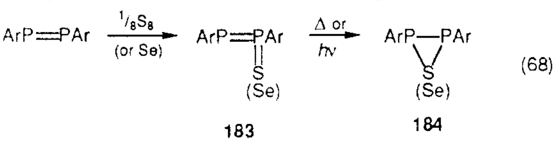
(66)

Cycloadditions have also been observed with germaphosphenes. For example, addition of sulfur or selenium to **167** leads to the corresponding three-membered rings **181a**[175] and **181b**[95,175] (eq 67). The first step of this reaction is probably the formation of germaphosphene sulfide or selenide **182**, which isomerizes rapidly to **181** due to the great affinity of sulfur or selenium for germanium (for example, Ge–Se = 115 kcal/mol).[186]

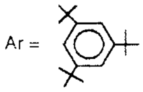


(67)

A similar mechanism has been postulated by Yoshifuji in the reaction of sulfur with diphosphenes: in this case the intermediate **183** is relatively stable and isomerizes slowly to the three-membered ring **184**[187] (eq 68).



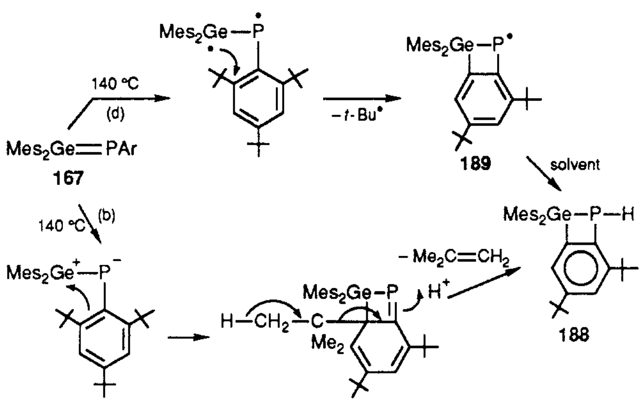
(68)

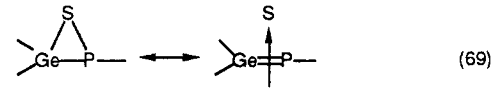


The X-ray structure of **181a** deserves some comments: germanium, phosphorus, and the three ipso carbons of the aromatic rings are nearly in the same plane with a quasi-planar germanium.[96] Surprisingly, the geometry of **181a** is very close to that observed in the starting germaphosphene **167**[166] (Figure 7).

So it seems that due to the planarity of the molecule (sum of angles on germanium = 358.1°) and the short Ge–P bond, the hybridization at germanium may be better represented as sp^2 than sp^3 and partial π bonding may exist between the germanium and the phosphorus atoms. The bonding may be intermediate between that of a normal three-membered ring and that of a π complex[96] (eq 69).

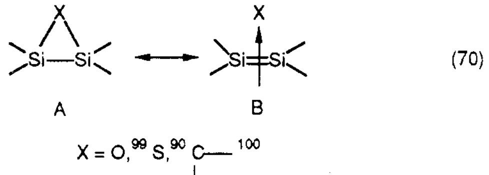
SCHEME 37





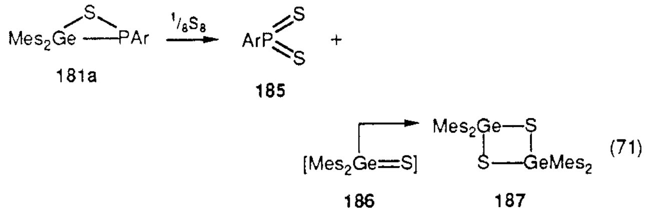
(69)

Similar observations have been made by West in the three-membered ring obtained from disilenes;[99] West postulated a contribution from the form B (eq 70). This hypothesis has been supported by calculations.[101]



(70)

Addition of an excess of sulfur to **181a** leads to metadithiophosphonate **185** and 2,4-digerma-1,3-dithietane **187**. The formation of **187** may involve a germanethione intermediate **186** (eq 71).



(71)

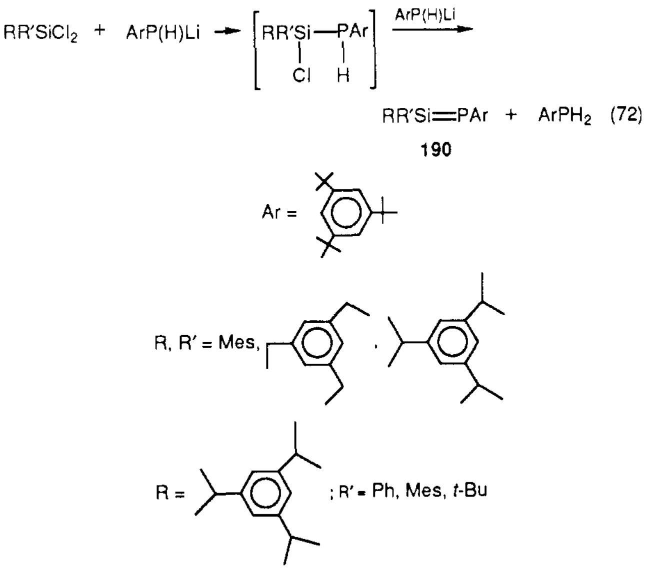
Thermolysis of **167** (140 °C/48 h) affords nearly quantitatively **188**, the unique stable germaphosphetene[173] (Scheme 37). X-ray analysis shows a nearly planar four-membered heterocycle. The formation of **188** may be explained by a radical process (route a) involving the preliminary formation of **189** by intramolecular radical aromatic substitution, followed by an abstraction of hydrogen from the solvent.[173] A similar aromatic substitution involving a silylated radical has been described by Ishikawa in the thermolysis of disilacyclopropanes.[188] However, route b or other routes for the formation of **188** are not excluded (Scheme 37).

(3) Sila- and Stannaphosphenes

(a) Silaphosphenes

Stable silaphosphenes **190** have also been recently synthesized and stabilized owing to bulky substituents on silicon and phosphorus.

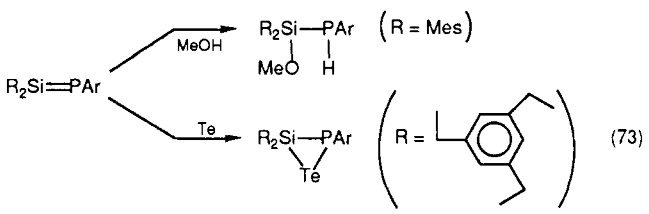
They were obtained by Bickelhaupt[189,190] from the reaction of ArP(H)Li and the corresponding dichlorosilanes RR′SiCl$_2$, followed by elimination of HCl. Depending on R and R′, several side reactions were encountered; for this reason and because of their instability, the compounds were not isolated in pure form (eq 72).



(72)

190

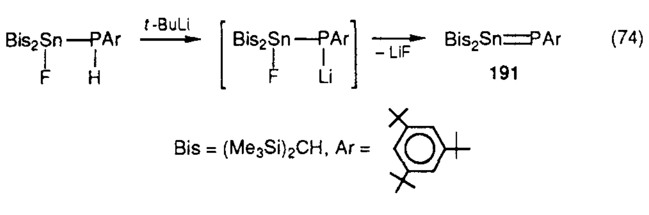
Silaphosphenes were characterized by their low-field ^{31}P and ^{29}Si NMR data, in the expected range for doubly bonded silicon and phosphorus, with a large ^1J(PSi) coupling constant: $\delta(^{31}P)$: 93–136 ppm; $\delta(^{29}Si)$: 148.7–175.9 ppm; ^1J(PSi): 149–155 Hz. They react very easily with methanol and tellurium[190] to give the corresponding adducts (eq 73).



(73)

(b) Stannaphosphenes

Only one stable stannaphosphene R$_2$Sn═PAr (**191**) has been stabilized so far in a monomeric state.[191] Compound **191** was synthesized by dehydrofluorination of the corresponding fluorostannylphosphine with *tert*-butyllithium (eq 74).

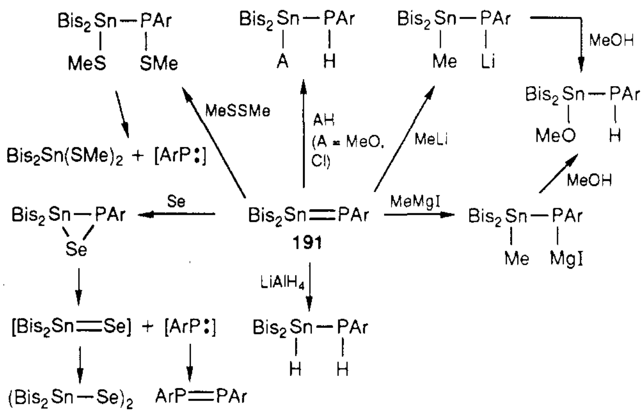


(74)

191

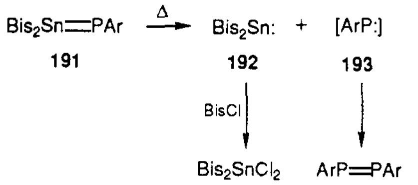
The stannaphosphene structure of **191** was unambiguously determined by NMR: the ^{31}P NMR chemical shift (+204.7 ppm) falls in the range of sila- and germaphosphenes. The ^{119}Sn chemical shift, at very low field (+658.3 ppm/Me$_4$Sn), is also a normal value for a tricoordinate pπ-hybridized tin. Similar chemical shifts have been observed in stannenes[71] and distannenes.[134] Very significant are the coupling constants between phosphorus and tin ($^1J(P^{117}Sn)$ = 2191, $^1J(P^{119}Sn)$ = 2195 Hz). These values are much larger than for single-bonded tin-phosphorus compounds (1150–1200 Hz), which can be attributed to a π bond between tin and phosphorus. A similar effect has been observed in the coupling constants, for example for $^1J(P^{29}Si)$ in silaphosphenes and ^1J(PP) in diphosphenes.

SCHEME 38



The structure of **191** was corroborated by its chemical behavior:[191,192] addition of protic reagents (alcohols,[185,191] hydrogen chloride[185,191]), lithio compounds, and Grignard reagents[185,192] to the double bond is regiospecific and confirms its expected polarity Sn$^{\delta+}$═P$^{\delta-}$. Reduction of the double bond by LiAlH$_4$,[185,192] addition of dimethyl disulfide,[185,192] and cycloaddition with selenium[185,192] are also observed (Scheme 38).

Thermolysis of **191** in a sealed tube at 70 °C for 15 h gives a completely different reaction from that observed in the case of germaphosphenes. It leads, probably according to a metathesis-type reaction, to the stannylene **192** and the phosphinidene **193**.[185,192] Evidence for the formation of **192** has been obtained by the thermolysis of **191** in the presence of BisCl, leading to Bis$_2$SnCl$_2$ (eq 75).



(75)

Reactions of stripping of halogens by divalent species of group 14 have already been observed by Neumann.[193] In the reaction between BisCl and stannylene **192** at room temperature, Lappert has observed the formation of Bis$_3$SnCl (**194**)[194] (eq 76).

$$\underset{192}{Bis_2Sn} + BisCl \longrightarrow \underset{194}{Bis_3SnCl} \qquad (76)$$

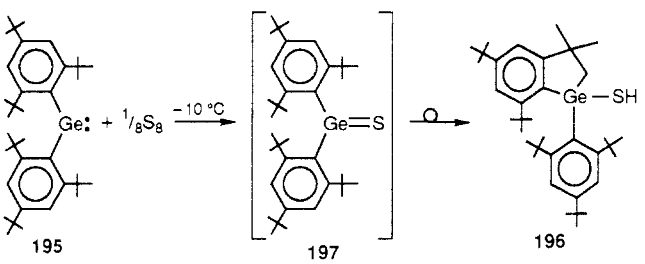
These two completely different reactions can be explained by a difference in the stannylene electronic state: singlet, which is the ground state of stannylene,[108,195] in the case of Lappert, and triplet when generated thermally from stannaphosphene.

VI. Ge═X (X = O, S) Species: Germanones and Germanethiones

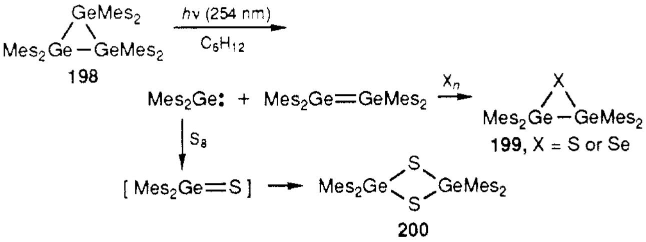
The chemistry of germanones and germanethiones is essentially the chemistry of elusive reactive intermediates.

Early work, summarized in a previous review,[6] was based on thermal generation of [>Ge═X] species (X

SCHEME 39



SCHEME 40



= O, S) by various β eliminations on linear germoxanes or germathianes, various cycloreversions, and oxygen or sulfur abstractions by germylenes.

A survey of the more recent results shows that no free germanone and only one compound with an intramolecular base-stabilized Ge–S double bond have yet been isolated. These [>Ge=X] species exhibit only fleeting existence under the experimental conditions used. Thus their preparation and their trapping, which are usually two aspects of the same experiment, often need to be described together. The only direct observation is based on a recent germanethione matrix isolation work.

(1) Transient Germanone and Germanethione Generation

Reaction of germylenes with oxygen or sulfur donors is an interesting reaction process which leads to germanones or germanethiones. In early work O_2, $KMnO_4$, DMSO, C_5H_5NO, and S_8 were the favorite oxidizing agents.[6]

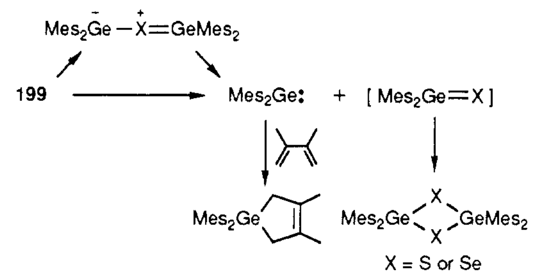
It is noteworthy that the adducts of germylene–transition-metal complexes of the type $Y_2GeM(CO)_5 \cdot THF$ (M = Cr or W, Y = F or Cl) with various 1,2-dipoles, aldehydes, oximes, and oxidizing agents (DMSO, C_6H_5NO, C_5H_5NO) present high stability that impedes their decomposition into [>Ge=X] intermediates.[196]

Bis[(2,4,6-tri-*tert*-butylphenyl)germylene] (**195**) is oxidized by elemental sulfur to give the germaindanethiol **196** apparently via the intermediate germanethione **197** by addition of an ortho *tert*-butyl group C–H bond to the Ge=S double bond[197] (Scheme 39).

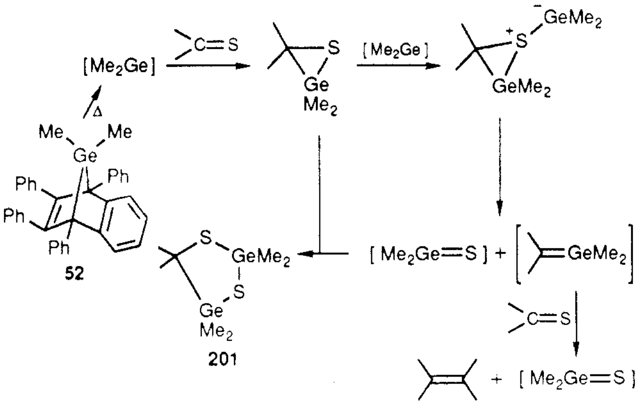
A route involving the reaction of dimesitylgermylene and sulfur to dimesitylgermanethione was suggested to explain the production of dithiadigermirane **199a** and dithiadigermetane **200** from irradiation of a cyclohexane solution of hexamesitylcyclotrigermane and elemental sulfur in a quartz tube at room temperature with a low-pressure mercury lamp.[86a] Similarly, selenadigermirane **199b** was obtained from the photolysis of **198** and selenium in cyclohexane at room temperature, but it is noteworthy that no adduct from dimesitylgermylene and selenium could be found (Scheme 40).

Photolysis of **199** (**a** and **b**) with 2,3-dimethyl-1,3-butadiene produces only products from dimesitylgermylene and dimesitylgermanethione or -selenone (Scheme 41).

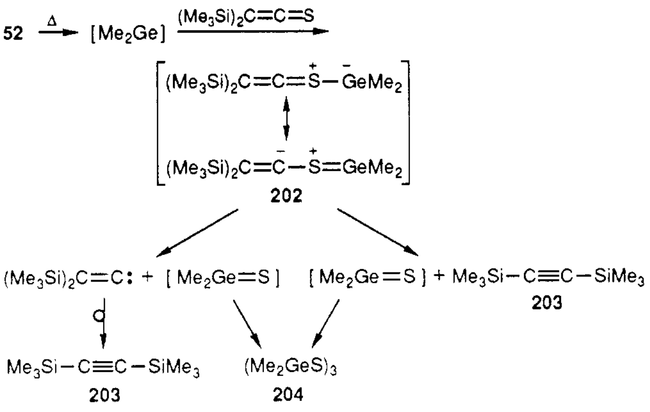
SCHEME 41



SCHEME 42



SCHEME 43

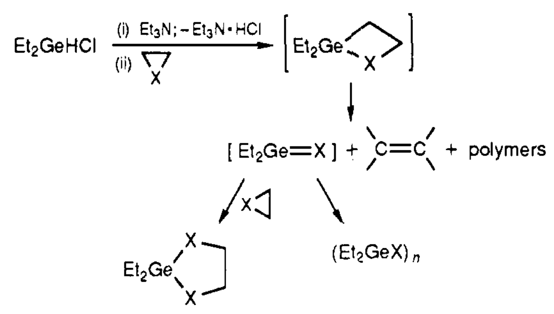


The intermediacy of free germanethione has been proposed to rationalize the results of the reaction of dimethylgermylene and thioketones[32,33] (adamantanethione and indanethione). Formation of 1,3,2,4-dithiadigermolanes **201** is explained by the authors in quite conventional fashion: dimethylgermylene adds to thioketone to form thiagermirane, which reacts with another molecule of germylene to eliminate sulfur to form dimethylgermanethione (Scheme 42).

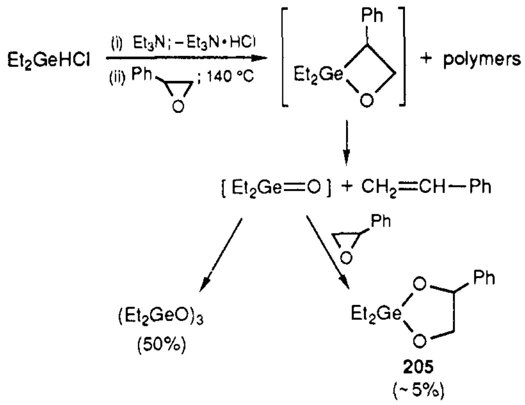
In the reaction of dimethylgermylene with bis(trimethylsilyl)thioketene, compounds **203** and **204** were obtained. Digermathietane or germathiirane are not formed in this reaction, in contrast with the reaction with di-*tert*-butylthioketene. The reaction proceeds probably by addition of germylene to thioketene to give the intermediate **202**, which decomposes directly to acetylenic **203** and germanethione or alternatively to germanethione and alkylidenecarbene[80] (Scheme 43).

Various germaoxetanes and -thietanes $R_2\overline{Ge{-}X{-}C{-}C}$ (X = O, S) are thermally unstable and lead probably via β elimination to transient dialkylgermanones and

SCHEME 44

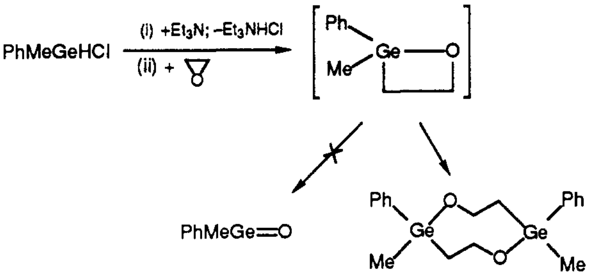


SCHEME 45



germanethiones, which can be trapped with oxirane or thiirane.[6,7] Reaction of chlorodialkylgermanes R_2GeHCl with (i) triethylamine in pentane (elimination of $Et_3N{\cdot}HCl$ by filtration) and (ii) various oxiranes and thiiranes is one of the recent methods investigated for the obtention of these four-membered heterocycles[198] (Scheme 44).

Evidence for the initial formation of germaoxetane or -thietane in these reactions was obtained when experiments starting from chloromethylphenylgermane were carried out with oxirane. In this case a rapid dimerization reaction of the transient germaoxetane occurs instead of decomposition to germanone (eq 77).



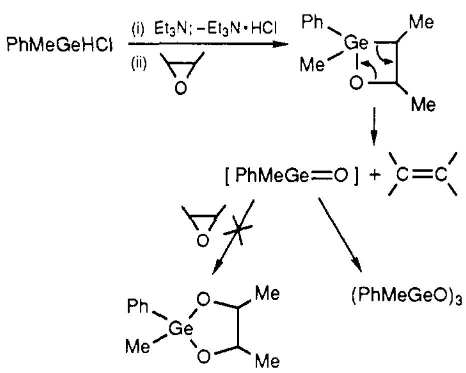
(77)

With phenyloxirane and chlorodiethylgermane as starting materials, the reaction leads to the germylated dioxolane **205** in low yield (~5%), the main reaction product resulting from formal germanone oligomerization (Scheme 45).

In the reaction of 1,2-dimethyloxirane with chloromethylphenylgermane as starting material, the formal germanone-trapping product is not obtained, suggesting a low reactivity of the methylphenylgermanone toward 1,2-dimethyloxirane (Scheme 46).

Thermolysis and pyrolysis of thiagermetane $Me_2\overline{GeCH_2SCH_2}$ (**206**) and photolysis of **206** and dithiagermolane $Me_2\overline{GeCH_2SSCH_2}$ (**207**) lead to various new germylated heterocycles, in particular **208**–**210**.[27,28]

SCHEME 46



Decomposition of **206** probably proceeds by two competitive mechanisms a and b (Scheme 47) involving transient germene $[Me_2Ge{=}CH_2]$, germanethione $[Me_2Ge{=}S]$, thiagermirane $Me_2\overline{GeCH_2S}$, and thiadigermetane $Me_2\overline{GeCH_2Ge(Me_2)S}$ (Scheme 47).

Path a, which is consistent with the observation by UV spectra of electronic interaction between sulfur and germanium in **206** and with the trapping of CH_2 by cyclooctene in these decompositions, seems to be predominant in thermolysis; path b, consistent with the mass spectrometric study of the decomposition of **206**, would be predominant in pyrolysis, but other possibilities clearly exist. These results indicate the possible occurrence of [2 + 2] cycloaddition between 1,1-dimethylgermene and dimethylermanethione.

For photolysis of **207** the authors proposed Scheme 48.

Pyrolysis of the thiagermetane dioxide $Me_2\overline{GeCH_2S(O_2)CH_2}$ is also postulated to involve multiply bonded germanium species: the germene $[Me_2Ge{=}CH_2]$ and probably the new doubly bonded germanium species, the germanesulfene $[Me_2Ge{=}SO_2]$, which finally gives germoxanes $(Me_2GeO)_n$ ($n = 3, 4$)[28] (Scheme 49). The germanesulfene has been detected in the mass spectroscopy of the four-membered-ring thiagermetane dioxide.

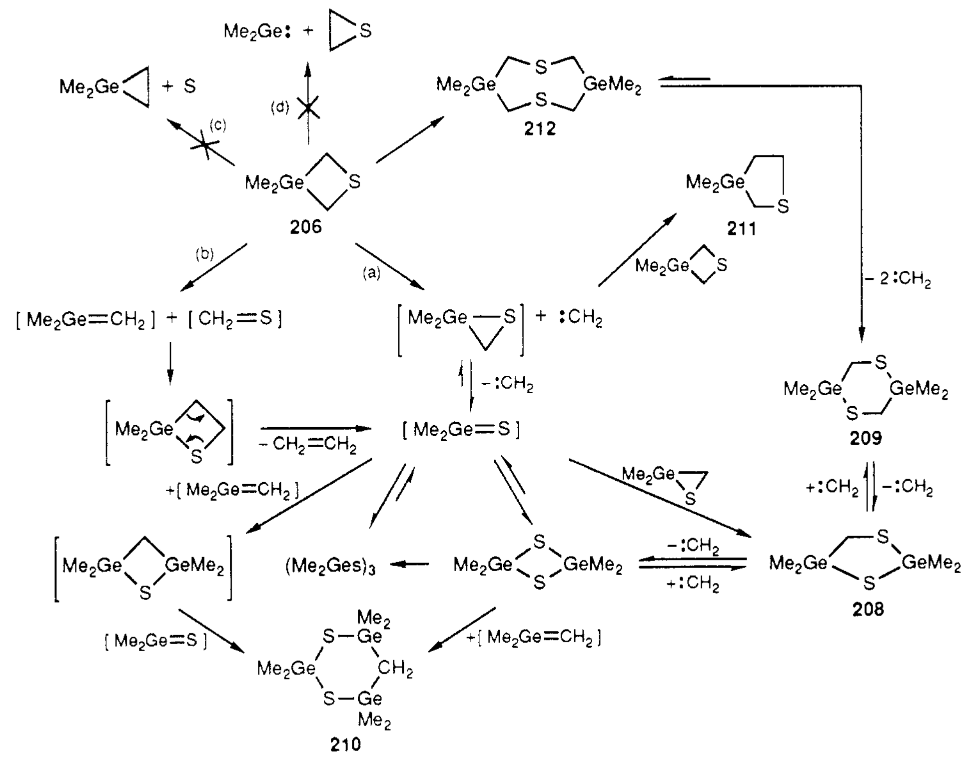
An interesting precursor for dimethylgermanethione and dimethylgermene seems to be the 2,4-digermathiane $Me_2\overline{GeCH_2Ge(Me_2)S}$ (**214**). This heterocycle, previously postulated as an intermediate in some thermolyses, is relatively stable in solution at room temperature but spontaneously dimerizes and easily dissociates upon heating.[30] Obtention of **215**–**217**, **210**, and $(Me_2GeS)_3$ supported the conclusion that germanethione and germene are both formed in this decomposition reaction (Scheme 50).

Dimethylgermanethione and a 1,1-dimethylgermene intermediate are also probably formed in the thermolysis of **215**. Obtention of **210**, **217**, and $(Me_2GeS)_3$ and the trapping reaction of $[Me_2Ge{=}CH_2]$ support these cycloelimination mechanisms (Scheme 51).

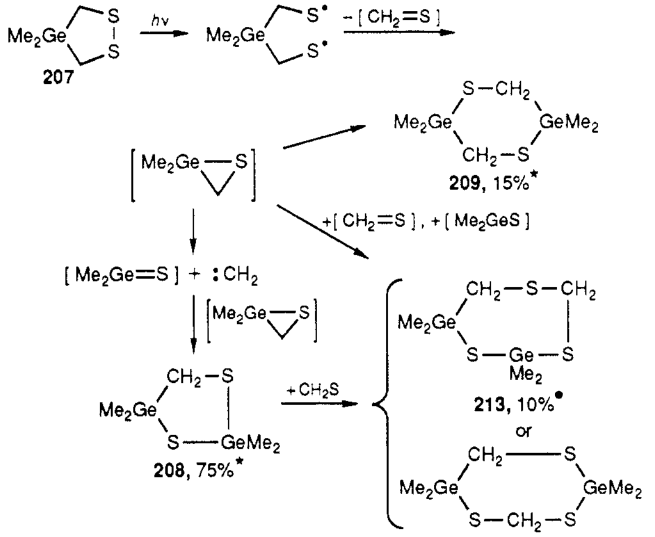
Similar decompositions of thia- or oxadigermetane intermediates **214** are postulated in investigations of the actions of S_8 or O_2 on the tetragermadimercurocane **218**[31] or on the [bis(dimethylgermyl)alkane]iron tetracarbonyls **219**[29] that, in a first step, lead to the relatively stable dithia- or dioxadigermolanes **220**[29,31] (Scheme 52).

It has been proposed that the decomposition of the phosphorylated heterocycle $Me_2\overline{GeSP(S)(An)S}$ (**221**),

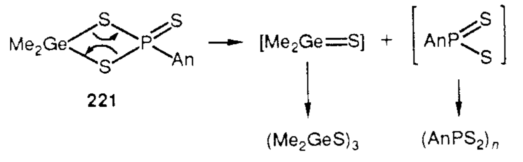
SCHEME 47



SCHEME 48



stable at room temperature, leads to the transient species [$AnPS_2$] and [$Me_2Ge{=}S$].[199] The evidence is the formation of the expected thiirane adducts of the germanethione and of [$AnPS_2$] when thiirane is present in the mixture. In the absence of trapping agent, $(Me_2GeS)_3$ and $(AnPS_2)_n$ are isolated from the reaction mixture (eq 78).



(78)

In the same way the dithiaphosphadigermolane **222** undergoes thermal fragmentation leading to $(Me_2GeS)_3$ and $(AnPS)_2$, probably via the monomer species [$Me_2Ge{=}S$] and [$AnP{=}S$].[199] The decomposition, which is inhibited in the presence of Et_3N, seems to be initiated by nucleophilic attack on germanium by the sulfur P=S. The dimethylgermathione can be trapped by $Me_2Ge(SMe)_2$ (Scheme 53).

The germathiaphosphirane **223** heated with an excess of sulfur leads to the metadithiophosphonate **224** and the 2,4-digerma-1,3-dithietane **225**. Three possible mechanisms involving formation of dimesitylgermanethione by decomposition of three- or four-membered heterocycles have been suggested to explain these formations[96] (Scheme 54).

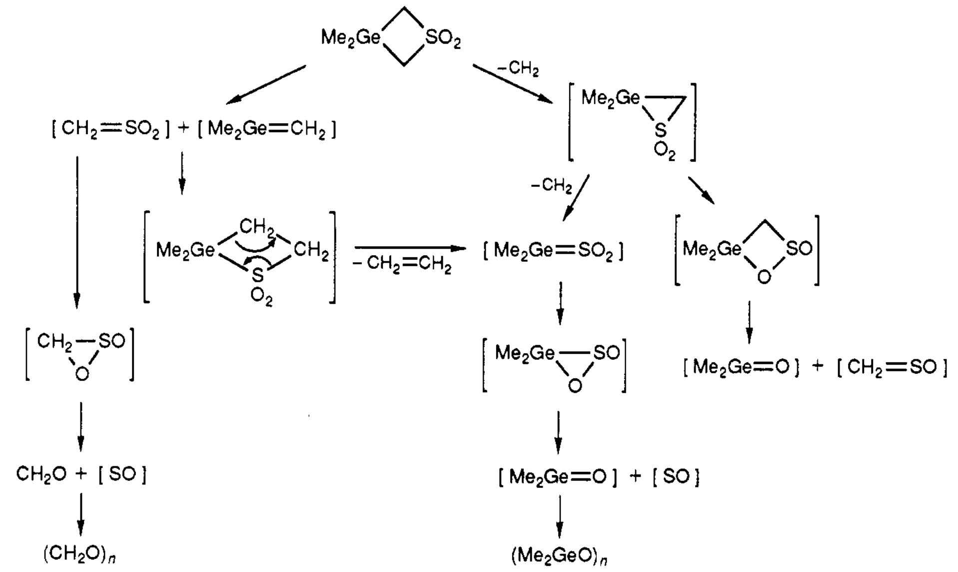
An interesting precursor to dimethylgermanone is the 1,3,2-dioxagermetane **226**, which is stable at room temperature in the solid state (association dimer form). Dilution or low pressures induce decomposition to form chloral and dimethylgermanone by β elimination. Dimethylgermanone is easily trapped by ethylene oxide or thiirane[200] (Scheme 55).

Decomposition in a similar manner of various dioxagermetane intermediates **227** has been suggested[200] (Scheme 56).

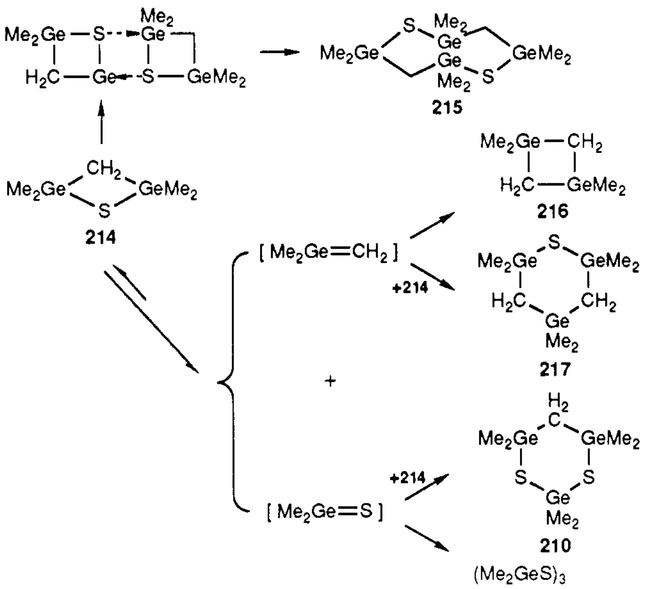
Dimethylgermanethione and dimethylgermylene are probably formed in the thermolysis of the 2,3-digerma-1,4-dithiane **228**, which leads to the isolation of the germylated heterocycles **229**–**231**.[201] The authors rationalize these results by two concurrent decomposition mechanisms of **228** involving formation of dimethylgermylene ([Me_2Ge:]) and dimethylgermanethione ([$Me_2Ge{=}S$]), respectively (Scheme 57). This proposal is supported by the result of the pyrolysis of **228** in the presence of 2,3-dimethylbutadiene: formation of the cycloadduct expected from the trapping of dimethylgermylene, the absence of **230** and **231**, and formation of the trimer of the dimethylgermanethione $(Me_2GeS)_3$ are observed in this experiment (Scheme 57).

Species [>Ge=X] (X = O, S) have been often suggested as intermediates formed in pseudo-Wittig reac-

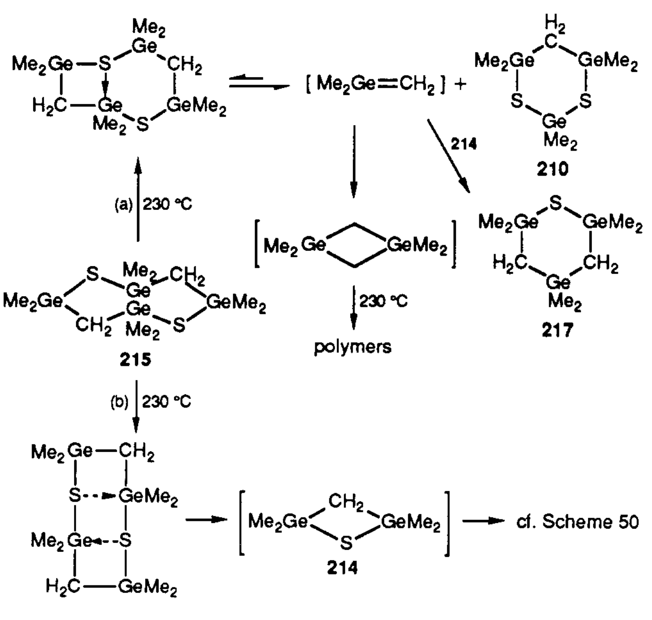
SCHEME 49



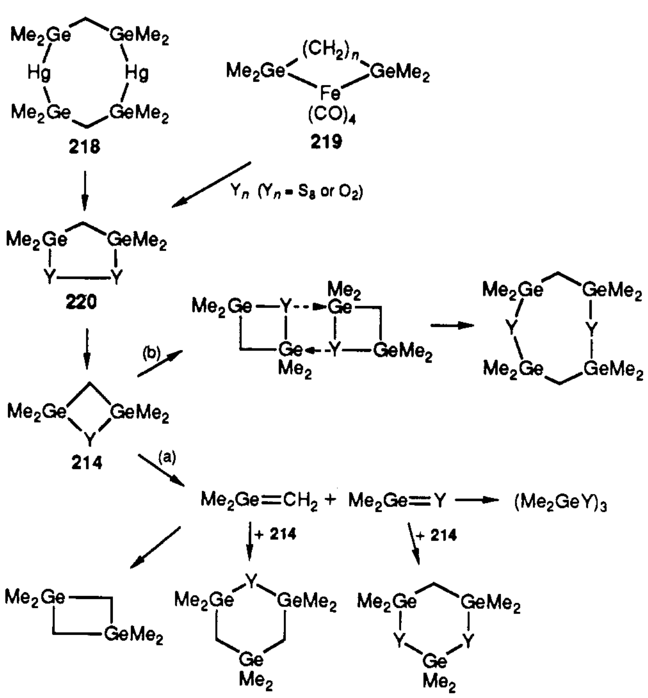
SCHEME 50



SCHEME 51

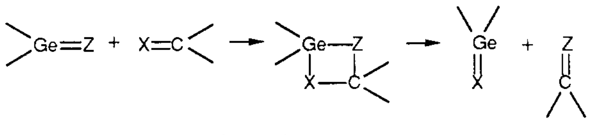


SCHEME 52ᵃ



ᵃa, Y = S; b, Y = O.

tions of germenes,[32,202] digermenes,[82] and germanimines[50,135-137,140] with carbonyl or thiocarbonyl compounds (eq 79). It is noteworthy that the adduct of

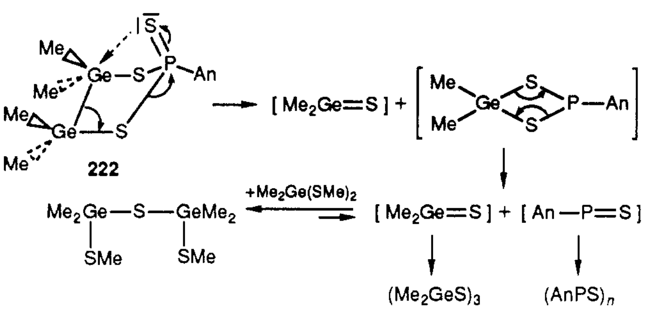


(79)

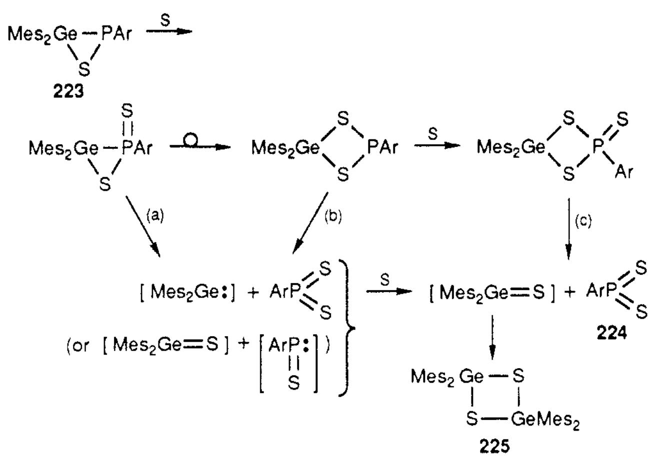
the germene **232** with Ph_2CO is not a source of dimethylgermanone.[25a] Thermal [2 + 2] or [2 + 4] cycloreversions of the isomers **22** and **233** regenerate **19** and Ph_2CO (cf. eq 5).

Direct generation of the dimethylgermanone from thermolysis in a flow system of the 6-oxa-3-germabicyclo[3.1.0]hexane **234** via a transient 2-germaoxetane

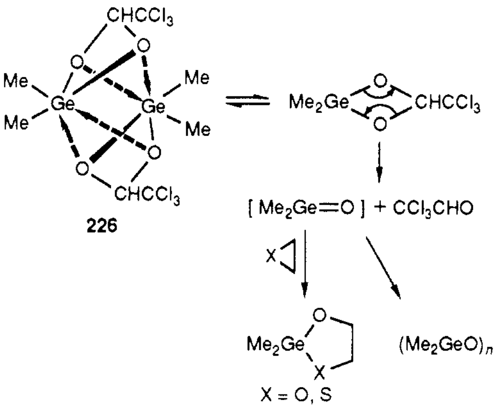
SCHEME 53



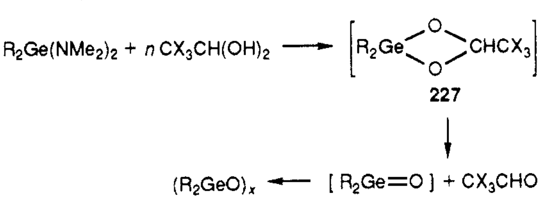
SCHEME 54



SCHEME 55



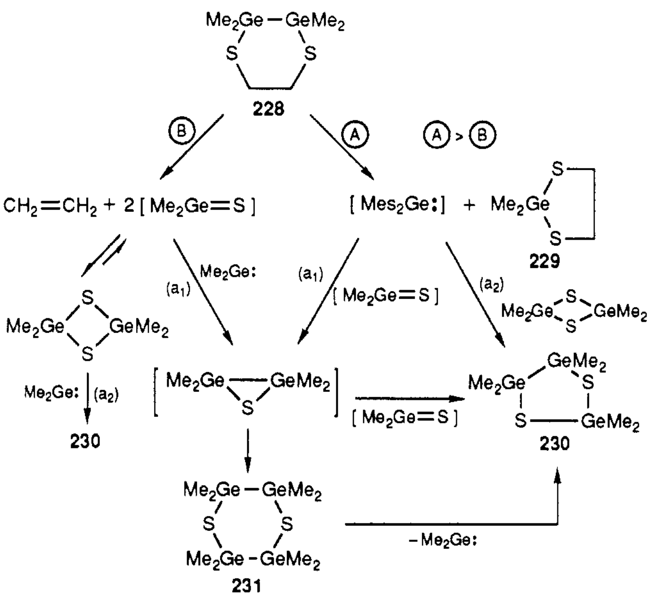
SCHEME 56



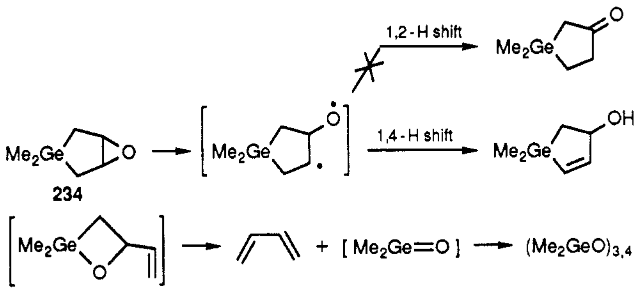
$n = 1$, R = Ph, X = Cl or F
R = Me, X = F
$n = 1$ or 2, R = NMe$_2$, X = Cl

has also been suggested. Initial formation of a diradical followed by attack on the metal atom by the oxygen radical with transient formation of an unstable germaoxetane that decomposes to germanone and 1,3-butadiene seems reasonable[203,204] (Scheme 58). The 1,4 hydrogen shift that gives rise to 3-germacyclopent-4-en-1-ol is a minor process and the 1,2 hydrogen shift that would lead to 3-germacyclopentan-1-one is not observed under the experimental conditions, where this derivative is stable (Scheme 58).

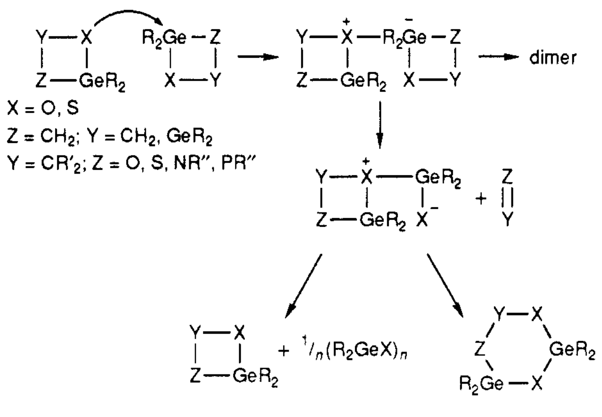
SCHEME 57



SCHEME 58

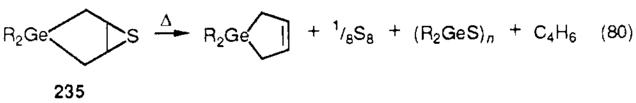


SCHEME 59



X = O, S
Z = CH$_2$; Y = CH$_2$, GeR$_2$
Y = CR'$_2$; Z = O, S, NR'', PR''

Similarly, thiiranes **235** are unstable and potential precursors of germanethiones[205] (eq 80).

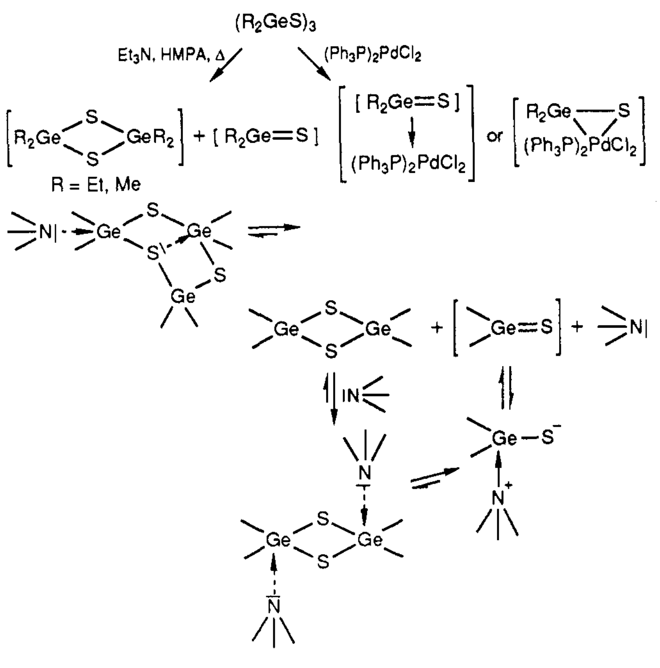


235

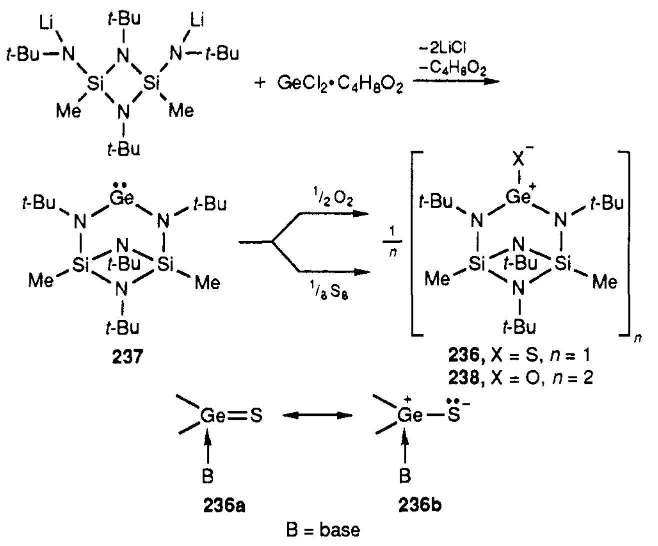
R = Me, 20 °C
R = Ph, 130 °C

It should be noted that in many of these reported reactions involving four-membered germylated rings, the data are compatible with mechanisms in which these strained heterocycles are believed to fragment to yield an olefin (a ketone, an imine, etc.) and a germanone or a germanethione, since the corresponding oligomers (R$_2$GeX)$_n$ (X = O, S; n = 3–5) are produced.

SCHEME 60



SCHEME 61



Similarly, intermediacy of free silanone has been postulated in reactions of the same type, particularly in the pyrolysis of oxasiletanes;[4] however, formation of these doubly bonded silicon species in these reactions has recently been questioned on the basis of calculations which suggest that the fragmentation of oxasiletanes is too endothermic to occur at a significant rate under pyrolytic conditions.[231] Thus, intervention of bimolecular mechanisms, such as those proposed for formation of the observed products in the pyrolysis of oxasiletane,[231] could be accepted too in the case of germanium (Scheme 59).

The intermediacies of germanones and germanethiones have also been often proposed to rationalize the results of thermal decomposition of various cyclogermoxanes and cyclogermathianes.

Cyclogermathianes $(R_2GeS)_3$ lead very easily, by thermal and catalytic dissociation, to the germanethiones $[R_2Ge{=}S]$.[206] Basic solvents such as Et_3N or HMPA and catalysts $(Ph_3P)_2PdCl_2$ induce these dissociations and catalyze the reaction of germanethiones with three- and four-membered rings (Scheme 60).

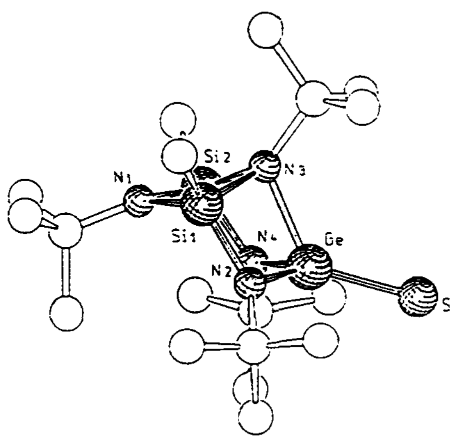
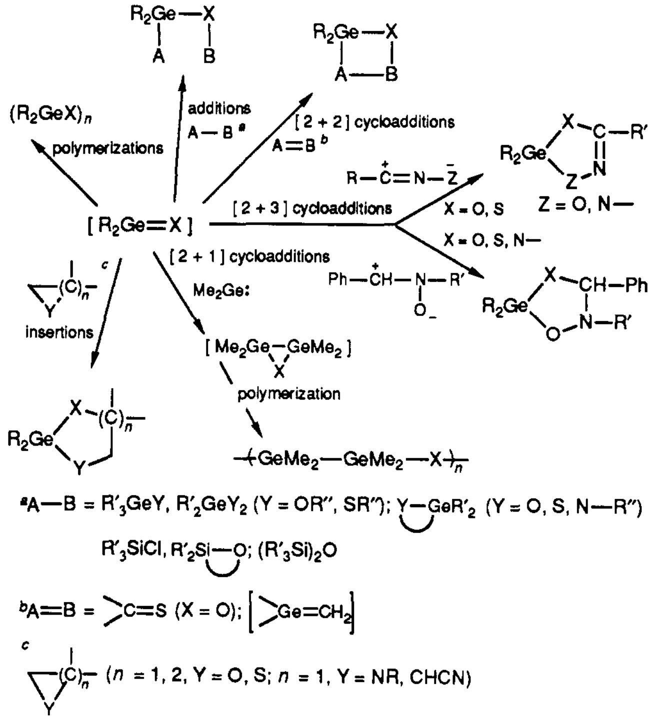


Figure 8. ORTEP view of **236** (reprinted from *Angew. Chem., Int. Ed. Engl.* 1989, *28*, 1238; copyright 1989 VCH Verlagsgesellschaft mbH).

SCHEME 62



Thermolysis of $(Me_2GeS)_3$ has been found to be useful for the production of matrix-isolated germanethione.[212]

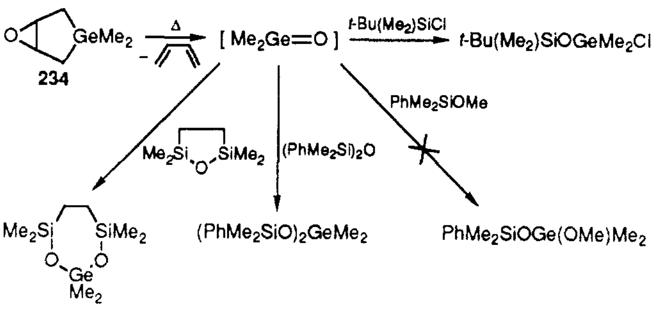
Germanones are often postulated as intermediates formed on thermal dissociation of various germoxanes;[200,206] the claims are supported by trapping experiments and ESR characterization (eq 81).

$$(R_2GeO)_n \underset{}{\overset{\Delta}{\rightleftharpoons}} (R_2GeO)_{n-1} + [R_2Ge{=}O] \qquad (81)$$

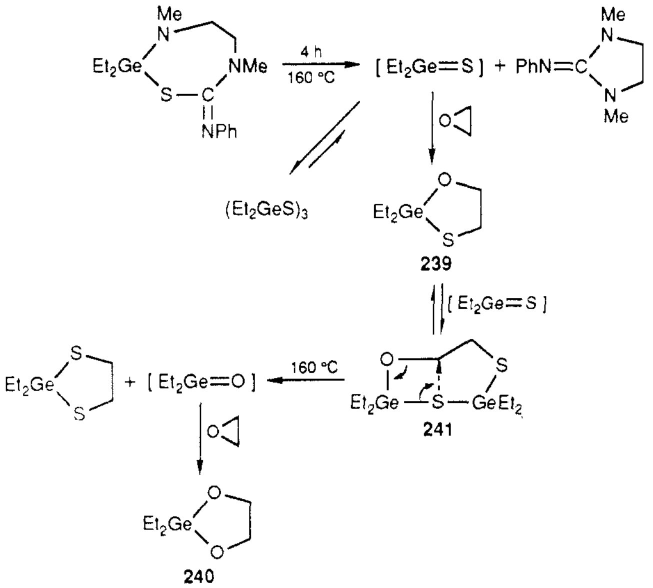
$$R = Me;\ n = 4$$
$$R = Me_3SiCH_2,\ Ph;\ n = 2$$

Recently, **236**, the first isolable compound with an intramolecular base-stabilized Ge–S double bond, has been reported.[232] Compound **236** is the sulfurization product of the bis(amino)germanediyl **237** (Scheme 61). In **236** the germanium atom is four-coordinate. The coordination can be described as distorted tetrahedral or as trigonal planar (N2, S, N4) with an additional bond (Ge–N3) (Figure 8). The Ge–S distance of 2.063 Å is about 0.2 Å shorter than the value of the Ge–S single bond, 0.06 Å shorter than the terminal Ge–S

SCHEME 63



SCHEME 64



distances in the thiogermanate ion $Ge_4S_{10}^{4-}$, and 0.05 Å longer than the calculated pπ–pπ Ge–S double bond in $Me_2Ge{=}S$. All these structural data suggest to the authors that a bonding model described in terms of the resonance structures **236a** and **236b** could be applied to this compound (Scheme 61).

Surprisingly, the oxidation product **238** of **237** is a dimer of the corresponding germanone.[232]

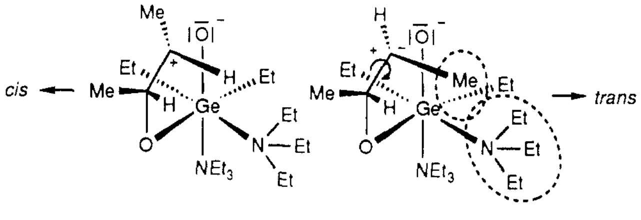
(2) Germanone and Germanethione Reactivity

Germanones and germanethiones with strongly polarized double bonds are highly reactive, and several kinds of reactions appear to be characteristic of these species: (i) polymerization reactions; (ii) addition reactions to various σ bonds of acyclic or cyclic organometallic compounds (e.g., Ge–O, Ge–S, Si–O, Si–Cl); (iii) insertion and expansion reactions with strained organic heterocycles; (iv) [2 + 2], [2 + 3], and [2 + 4] cycloaddition reactions (Scheme 62).

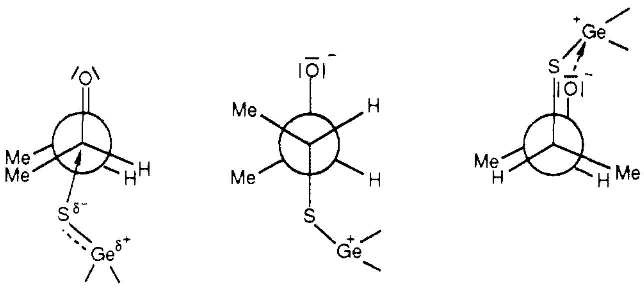
Insertions of [>Ge=X] into simple bonds between an atom carrying a lone pair and a group 14 metal are facile. Many of these reactions are postulated for Ge (se above or refs 6, 7, 27, 28, 30, 32, 33, and 199). Insertions of dimethylgermanone into Si–O and Si–Cl bonds are also observed,[204] Si–O bonds of siloxanes being more reactive than Si–O bonds of alkoxysilanes toward insertion of dimethylgermanone (Scheme 63).

The addition of a C–H function from the ortho *tert*-butyl group of an intermediate germanethione to the Ge=S bond has also been postulated[197] (cf. Scheme 39).

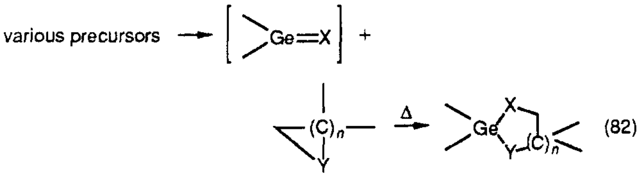
SCHEME 65



SCHEME 66



As examples of reactions with small organic rings, we summarize the results of the work quoted in ref 206. Dialkylgermanones and dialkylgermanethiones [$R_2Ge{=}X$], directly generated from various heterocyclic precursors and dimeric or trimeric forms $(R_2GeO)_2$ and $[R_2GeS)_3$, react with various three- or four-membered rings $Y(CH_2)_n$ to lead to the germaheterocycles $R_2GeY(CH_2)_n$ (n = 2 or 3) (eq 82).

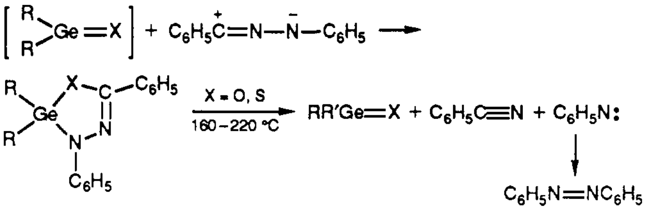


Y = O, S; NR, CHCN; n = 2
Y = O, S; n = 3

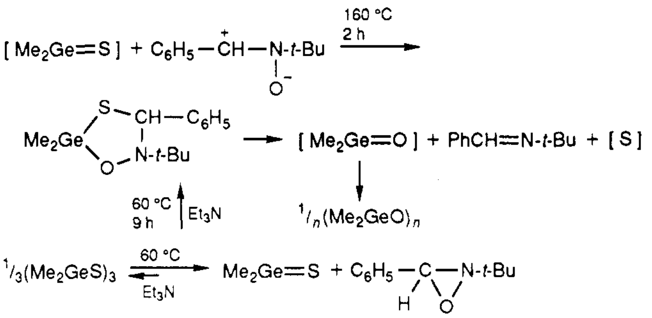
Simultaneous obtention of oxathiolane **239** and dioxolane **240** as final products is observed in the reaction of diethylgermanethione with oxirane at 160 °C (cf. Scheme 64). When the reaction is carried out at lower temperature (100 °C) with $(Et_2GeS)_3$ as the precursor of [$Et_2Ge{=}S$], the oxathiolane **239**, expected from the trapping of [$Et_2Ge{=}S$] with the oxirane, is the only adduct recovered. It is assumed that formation of an intermediate germanone [$Et_2Ge{=}O$] originating from the decomposition of adduct **241** is probably responsible for **240**. Such decomposition being detected in a separate experiment (decompositions of the adduct dimethylgermanone [$Me_2Ge{=}O$]–diethylgermadithiolane $Et_2GeSCH_2CH_2S$), Scheme 64 is proposed as a working hypothesis for the mechanism of this reaction.

The mechanism and the stereochemistry of some of these additions to small rings have been studied.[198] The condensation reactions of germanone with oxirane begin by nucleophilic attack of oxygen on germanium, followed by ring opening and cyclization. This nonconcerted mechanism is supported by the results of condensation of the germanone with cis or trans isomers of butene oxide. Each reaction leads to a mixture of cis and trans adducts: 45/55 from *cis*-butene oxide and 52/48 from *trans*-butene oxide. However, in the presence of triethylamine, the percentage of the cis adduct increases. In the presence of a 300% excess of

SCHEME 67



SCHEME 68



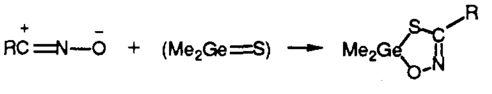
triethylamine, almost exclusive formation of the cis adduct is observed from both *cis*- and *trans*-butene oxide, along with a maximum of 2% of the trans adduct.

The high stereoselectivity in the presence of triethylamine implies a germanium atom hexacoordinated by two molecules of triethylamine. The study of molecular models shows very strong steric interactions between the methyl group and the triethylamino group in the equatorial position of the bipolar intermediate during the cyclization process. The position of least hindrance occurs when the two methyls are in the cis position opposite the triethylamino group, leading to the cis isomer (Scheme 65).

On the other hand, the condensation of germanethione with *cis*- or *trans*-butene oxide gives a stereospecific reaction with inversion of configuration: *cis*- and *trans*-butene oxides lead to trans and cis adducts, respectively, in proportions >95% with or without triethylamine.[198]

The mechanism of this reaction seems to proceed by nucleophilic attack of sulfur on the epoxide with configuration inversion (Scheme 66).

New cycloaddition reactions with 1,3-dipolar reagents (nitrilimines, nitrones, and nitrile oxides) have been observed.[207,208] The reactions of germanone and germanethione with diphenyl-2,5-tetrazole (precursor of nitrilimine) gave regioselective cycloaddition with formation of germaoxa- or germathiadiazolines (Scheme 67). Dimethylgermanethione reacts with nitrones (diphenylnitrone and phenyl-*N*-*tert*-butylnitrone) to form germaoxathiazolidines. Dimethylgermanethione reacts with butylphenyloxazirane (isomer of phenyl-*N*-*tert*-butylnitrone) by an insertion reaction in the oxazirane ring and formation of the same germaoxathiazolidine[208] (Scheme 68). Nitrile oxides also give cycloadducts with germanethiones[208] (eq 83). The regioselectivity of all the 1,3-cycloaddition reactions is analogous to that observed with ketones, thioketones, or CS_2.[209]



(83)

R = Ph, mesityl

(3) Calculations

Ab initio calculations using pseudopotentials have been carried out on $H_2Ge{=}O$ and $H_2Ge{=}S$. The geometries of the lowest singlet and triplet states of the doubly bonded molecules as well as the geometries of their respective singlet germylenes have been optimized at the SCF level of theory.[26,210] Singlet $H_2Ge{=}X$ (X = O, S) compounds possess a planar structure, while the corresponding triplets are both twisted and pyramidalized on germanium (for charge density and density difference contour maps for the π MO of germanone and of germathione, see refs 6 and 210). Germanone and germanethione are predicted to have singlet ground states; the results are also obtained with MNDO methods.[211] The lowest triplet state of H_2GeO is 44 kcal/mol higher in energy than the singlet (determined by CI calculation). H_2GeO: Ge–O = 1.634,[26,210] 1.611 Å,[211] Ge–H = 1.547,[26,210] 1.499 Å,[211] ∠HGeO = 124°,[26,210] 119.4°;[211] $\nu_{Ge=O}$ = 1036 (SCF),[26] 881 (CI),[26] 980 cm^{-1} (MNDO);[211] μ = 4.65 D. H_2GeS: Ge=S = 2.020 Å, Ge–H = 1.55 Å, ∠HGeS = 125°; $\nu_{Ge=S}$ = 586 cm^{-1}; μ = 3.80 D.

The Ge=X bonds are strongly polarized, especially in $H_2Ge{=}O$. The σ and π Ge–O bond polarities suggest that the bonding is intermediate between $\pi(H_2Ge{=}O)$ and semipolar $(H_2Ge{:}\rightarrow O)$ bonding.

The reaction enthalpies of $H_2GeX \rightarrow H_2Ge(^1A_1) + X(^3P)$ are about 108 kcal/mol for X = O and 83 kcal/mol for X = S.

For each case singlet germylenes are calculated to be more stable than their π-bonded isomers (by 20 kcal/mol in the case of germanone at the CI level).

Recently ab initio Hartree–Fock level calculations have been carried out on $Me_2Ge{=}S$.[212] The calculated equilibrium geometry is of C_{2v} symmetry. Me_2GeS: Ge=S = 2.010 Å, Ge–C = 1.950 Å, ∠CGeC = 110°; $\nu_{Ge=S}$ = 666 cm^{-1} (599 cm^{-1} after scaling correction); μ = 4.6 D.

(4) Photoelectron Spectroscopy

Pyrolytically produced germanones and germanethiones have been investigated by photoelectron spectroscopy (PES). The PES spectra of the trimer of dimethylgermanethione, $(Me_2GeS)_3$, were analyzed between 80 and 300 °C.[213-215] The spectrum recorded at 300 °C is interpreted in terms of a decomposition of the trimer and a coexistence of dimer and monomer. A very intense band in the spectrum at 8.6 eV is assigned to the ionization of the nonbonding pair on sulfur in the dimethylgermanethione. Bands at 9.55, 10.75, and 11.47 eV are characteristic of π ionizations of the Ge=S bond, the Ge–S bond, and the Ge–C bond, respectively.

The spectrum of $Me_2\overline{GeOCH(CCl_3)O}$ decomposition products includes the characteristics of the chloral and of the dimethylgermanone whose ionization potentials are 9.7 (n_O), 10.2 ($\pi_{Ge=O}$), 11.0 (σ_{Ge-O}), and 12.1 eV (σ_{Ge-C}).[215,216]

At temperatures higher than 150 °C the monomer apparently recombines as a result of thermal agitation, yielding the stable trimer $(Me_2GeO)_3$. This explains why only the trimer is visible in the photoelectron spectrum when the tetramer $(Me_2GeO)_4$ is decomposed at 350 °C.

TABLE 9. Vibrations of Dimethylgermanethione

obsd vib[a]	assignment
850 (s)	CH_3 rock (in phase)
605 (vs)	Ge=S stretch
1390 (m)	CH_3 asym def (in phase)
761 (m)	CH_3 def (in phase)
1229 (m)	CH_3 def (out of phase)
753 (m)	CH_3 rock (out of phase)

[a] Frequency in units of cm^{-1}.

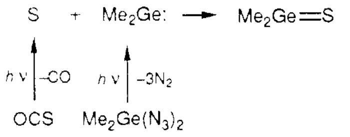
All these assignments are in agreement with theoretical ionization potentials calculated with the PS HONDO program and introduced polarization and correlation interpair corrections.

The observed ionization potentials are interpreted in terms of the highly polar character of the $\pi_{Ge=O}$ and $\pi_{Ge=S}$ bonds. This polarization and the relatively low ionization potentials explain the very high reactivity of these species and their short lifetimes.

(5) Matrix-Isolated Dimethylgermanethione

Recently, the IR spectrum of the matrix-isolated dimethylgermanethione obtained by gas-phase pyrolysis of $(Me_2GeS)_3$ was reported.[212] The observed frequencies and their relative intensities (cf. Table 9) are in good agreement with those calculated at the ab initio Hartree–Fock level.

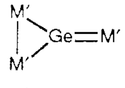
The same IR spectrum is obtained by interaction between atomic sulfur and dimethylgermylene obtained by photodecomposition of OCS and $Me_2Ge(N_3)_2$, respectively[212] (eq 84).



(84)

VII. Ge=Mn Species

The significantly shortened Ge–M_T distance and the trigonal-planar environments at the germanium atom in the complexes LM←GeXY may indicate the presence of a formal double bond in these derivatives. Chemical properties and the most important spectroscopic features of these complexes of divalent germanium are well summarized in a recent review;[217] we report here only recent works concerning structures **242–245**[218-221] for which X-ray diffraction studies[218,219,221] and theoretical calculations[222] clearly revealed multiple-bond character.



242, M' = $(\pi^5\text{-}C_5H_5)Mn(CO)_2$[218,219]

243, M' = $(\pi^5\text{-}C_5H_4Me)Mn(CO)_2$[220]

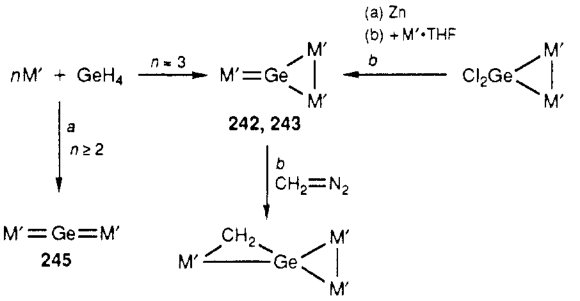
M'=Ge=M'

244, M' = $(\pi^5\text{-}C_5H_4Me)Mn(CO)_2$[220]

245, M' = $(\pi^5\text{-}C_5Me_5)Mn(CO)_2$[221]

The synthesis of compounds **242** and **245** is achieved by treatment of the solvent complex M'(THF) with germane (GeH_4) in the presence of sulfuric acid (Scheme 69). Compounds **243** and **244** have been obtained by treatment of $K[(\pi^5\text{-}C_5H_4Me)Mn(CO)_2GeH_3]$ with Hg^{2+} ions and acetic acid, respectively.[220] Diazomethane reacts with **242** with addition of CH_2 to the Mn=Ge multiple bond.

SCHEME 69



[a] M' = $(\pi^5\text{-}C_5Me_5)Mn(CO)_2$. [b] M' = $(\pi^5\text{-}C_5H_5)Mn(CO)_2$.

X-ray analyses[219,223] show a strictly linear Mn–Ge–Mn skeleton for compounds **244** and **245**. In these compounds the manganese–germanium bonds lengths average 2.18–2.20 Å and thus correspond to considerable multiple bonding between these atoms (2.48–2.60 Å for single bonds).

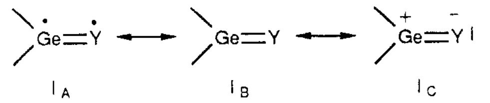
VIII. Conclusion

Although the chemistry of doubly bonded germanium species remains in some cases that of elusive intermediates, it appears, upon comparison of the present review with the previous review of multiply bonded germanium species,[6] that progress in the field during the past 8 years has been important, particularly in the field of stable or stabilized doubly bonded species.

The first stable germenes, digermenes, germaphosphenes, germanimines, and germanethiones have recently been isolated. Digermenes and germaphosphenes were kinetically stabilized owing to steric hindrance, which prevents oligomerization. In the cases of germenes and germanimines both steric and mesomeric effects can act as factors for stabilization. A germanethione was stabilized by intramolecular coordination of a base, and dimethylgermanethione ($Me_2Ge=S$) has recently been characterized at low temperature by matrix techniques.

The structure of various stabilized germenes, digermenes, germaphosphenes, and germanethione has been proved by X-ray analyses which show a planar or a nearly planar germanium and a shortening of the double bond by 8–10%. This shortening is less than that observed between alkanes and alkenes (13%) but comparable to the shortening previously reported for other doubly bonded main-group species such as silenes, disilenes, phosphenes, diphosphenes, and diarsenes.

A >Ge=Y species can be considered as a hybrid of the following three resonance structures:



I_A I_B I_C

On the basis of the physical and chemical properties, it appears that structure I_C seems to make the greatest contribution in the cases of asymmetrical structures (Y = O, S, N–, C<) while structure I_A seems to be predominant in the cases of symmetrical (Y = Ge<) or asymmetrical structures when the electronegativity difference between the two bonded atoms is low (Y = P–). The doubly bonded germanium structure is favored by mesomeric effects of the ligands (aromatic groups on germanium or on Y) while the biradical structure is favored by the donor inductive effect of the ligands.

Reports of chemical trapping of doubly bonded germanium species are numerous, but detailed reaction mechanisms are known for only a few of the reactions of this family. In many reactions, formation and reactivity of free >Ge=Y have been postulated and a variety of reaction mechanisms have been proposed.

A statement that can be made with considerable certainty is that the polar character of Ge–Y multiple bonds leads to numerous types of reactions (insertion, addition, cycloaddition, transposition, etc.). Moreover, the symmetrical structure of some species and the weaker polar character of other ones leads also in some cases to radical activity. However, the experimental evidence that is presently available does not provide a basis upon which to decide between the possible alternatives. Calculations would be of particular importance in some cases for the interpretation of experimental data.

The new "organometallic functions" >Ge=Y (Y = C<, N–, O, P–, Ge<, M) are much more reactive than the carbon analogues and are precursors to many new formulations in germanium–heteroelement chemistry. Moreover, these unsaturated species could be interesting precursors of new high-performance materials of practical interest such as polymers, conductors, and ceramics.

The synthesis and investigation of the chemical properties of novel structures containing sp germanium such as –Ge≡X, Y=Ge=Y are likely to be the next challenge in organogermanium chemistry.

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