

Organogermanium species with the metal in low coordination states. Recent results from the Toulouse group

Jacques Satgé

*Laboratoire de Chimie des Organominéraux, URA 477 du CNRS Université Paul Sabatier,
 118 route de Narbonne, 31062 Toulouse Cedex (France)*

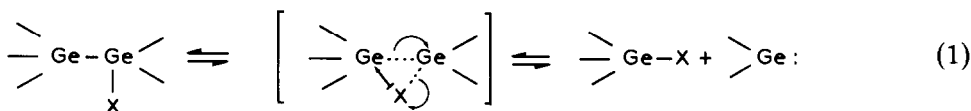
(Received July 25th, 1990)

In recent years there have been considerable interest in and numerous investigations of organometallic species or intermediates with a metal with an unusual degree of coordination. These species are of great interest from the fundamental, theoretical, and synthetic points of view. Several recent articles or reviews have portrayed the rapid development of research in the field of organometallic intermediates species of group 14 [1–11]. The contribution of Toulouse group in this field and especially in organogermanium chemistry is important [1–3].

This article presents our more recent results in the field of the chemistry of germylene and multiply-bonded germanium species.

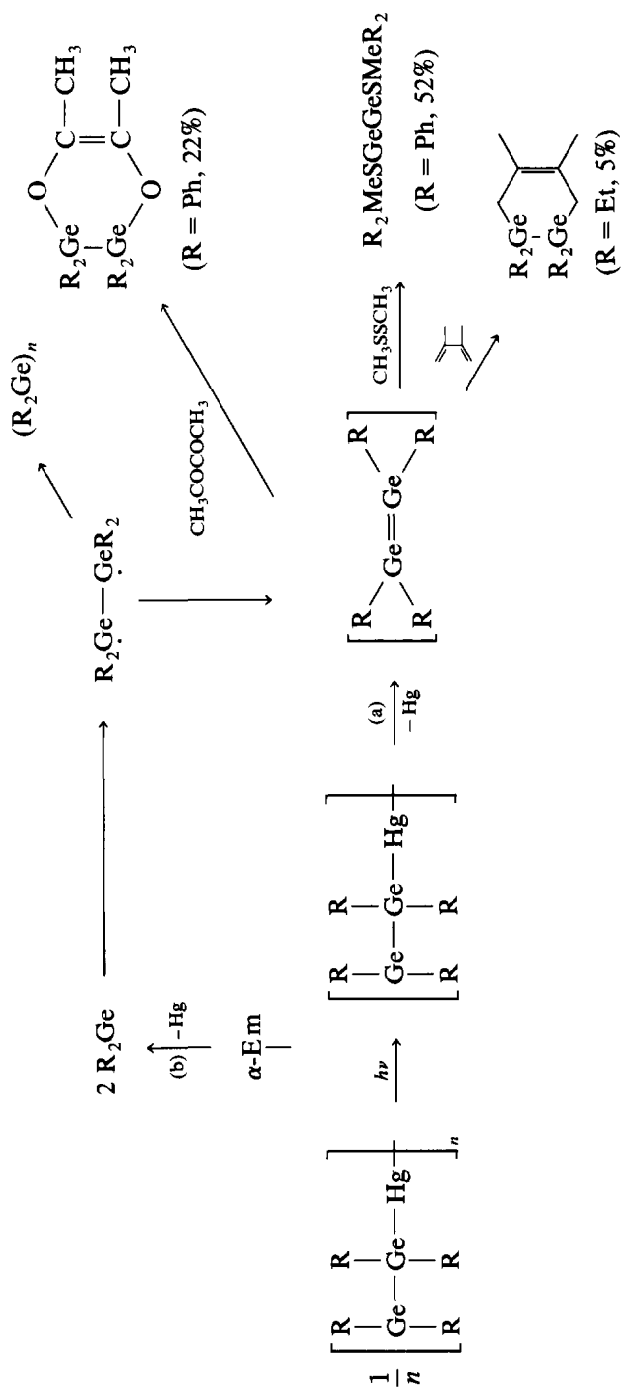
Germynes

Several thermal or photochemical α -elimination reactions of functional polygermanes lead to germynes R_2Ge [12] (eq. 1).



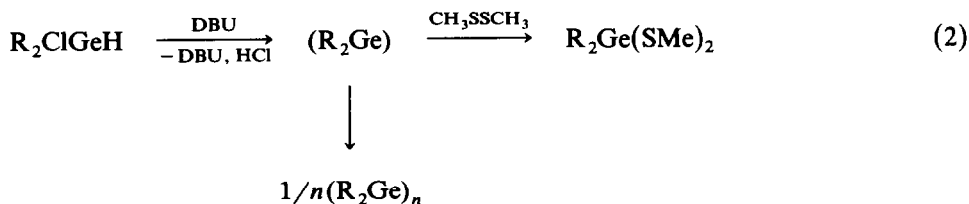
Photolysis of polygermanes, cyclopolygermanes and polygermylmercury compounds and also hydrogen abstraction from various organohydropolygermanes by $t\text{-BuO}^\bullet$ lead to the formation of a polymetallated chain containing one or two germanium centered radicals. These polygermyl radicals give germynes R_2Ge , germanium centered radicals >Ge^\bullet , α -digermyl diradicals (or digermenes), $[\text{>Ge} - \text{Ge} \leftrightarrow \text{>Ge} = \text{Ge} \langle]$, and β - or γ -polygermyl diradicals via a homolytic monoelectronic α -elimination process. In some cases the formation of α -digermyl diradicals or digermenes can also be seen as occurring through dimerization of germynes.

All these intermediates have been characterized by several trapping reactions with dimethyldisulfide, 2,3-dimethylbutadiene or biacetyl [12] (Scheme 1).



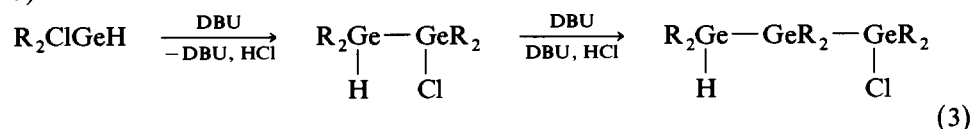
Scheme 1

The hydrides PhCl_2GeH and R_2ClGeH are dehydrochlorinated by DBU (1,8-diazabicyclo[5.4.0]undec-7-ene) to give germylene [13] (eq. 2)



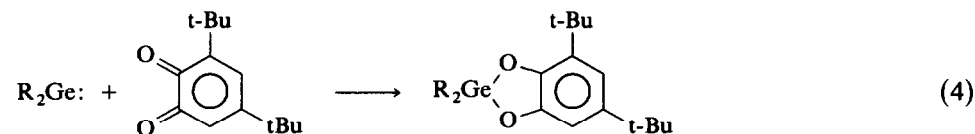
$\text{R} = \text{Et, Ph, Mes}$

When these reactions are carried out in concentrated solutions, intermolecular reactions predominate and give organochlorohydropolygermanes in good yields (eq. 3)



The latter reaction provides an interesting and selective way of obtaining digermanes with bulky substituents ($\text{R} = \text{mesityl}$). In these reactions, the formation of di- and tri-germanes can be explained in terms of the intermediate formation of germylene [13].

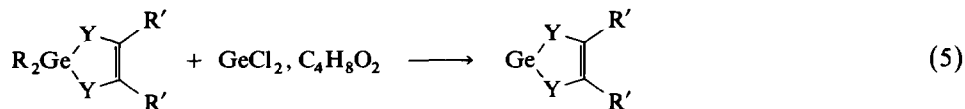
The germylenes X_2Ge , RGeX and R_2Ge ($\text{X} = \text{halogen, OR}$; $\text{R} = \text{alkyl or aryl}$) react at room temperature with 3,5-di-*t*-butyl orthoquinone by regioselective cycloaddition [14]. The corresponding substituted 2-germa-1,3-dioxolanes are formed in good yields (eq. 4)



Their stabilities depend on the substituents on the metal. Thus 2-halo(6,8-di-*t*-butyl)4,5-benzo-2-germa-1,3-dioxolans undergo redistribution reactions while the corresponding dialkyl or diaryl derivatives are very stable [14]. Reactions of the same type have been described by Neumann for dimethylgermylene [15].

The hitherto unknown germanium(II) pseudohalides $\text{Ge}(\text{CN})_2$, $\text{Ge}(\text{NCO})_2$ and $\text{Ge}(\text{NCS})_2$ have been prepared by reactions of germanium(II) halides with corresponding silver or potassium salts. They are stable in tetrahydrofuran or acetone but extremely sensitive to moisture. They undergo cycloadditions with 2,3-dimethylbuta-1,3-diene or 3,5-di-*t*-butyl-orthoquinone, insertion reactions with $[\text{FeCp}(\text{CO})_2]_2$ or dimethyldisulfide, and Lewis acid-base complexation reactions with DBU or α, α' -bipyridine, characteristic of highly reactive germylenes. Infrared spectroscopy indicates that, in tetrahydrofuran solution, $\text{Ge}(\text{CN})_2$ is the normal cyanide, whereas $\text{Ge}(\text{NCO})_2$ and $\text{Ge}(\text{NCS})_2$ are the isocyanate and isothiocyanate respectively [16].

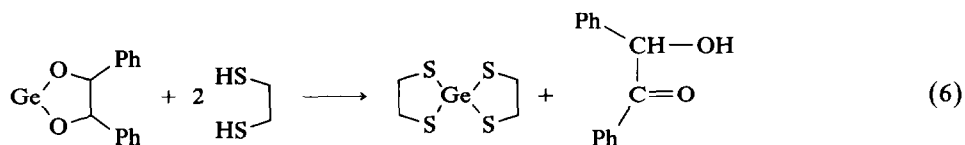
The exchange reactions between dithia- and dioxagermole with GeCl_2 , dioxane give new stable unsaturated germylene [17,18] (eq. 5).



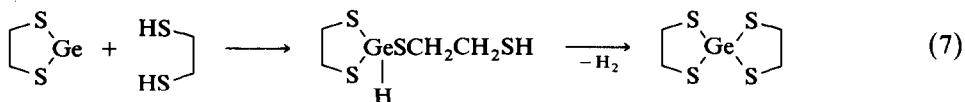
$\text{Y} = \text{S}, \text{R}' = \text{H}, \text{CN}, \text{R} = \text{Me}, \text{Et}, \text{Ph}$

$\text{Y} = \text{O}, \text{R}' = \text{Ph}, \text{R} = \text{Et}, \text{Ph}$

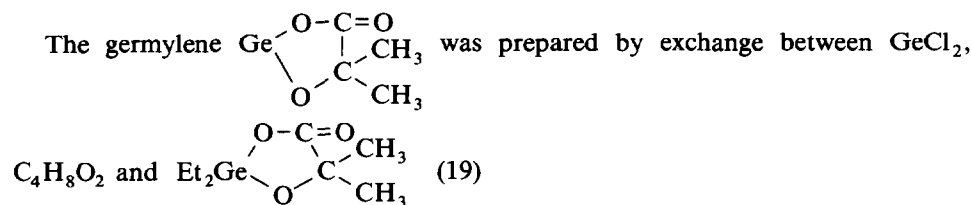
The germylene $\text{Ge} \begin{array}{c} \text{S} \text{CN} \\ \diagup \text{C} \\ \diagdown \text{S} \text{CN} \end{array}$ can also be obtained by reaction of $\text{GeCl}_2, \text{C}_4\text{H}_8\text{O}_2$ with $\text{NaSC}(\text{CN})=\text{C}(\text{CN})\text{SNa}$. The 4,5-diphenyl-1,3-dioxa-2-germole has been characterized by mass spectroscopy and by reaction with ethanedithiol (eq. 6).



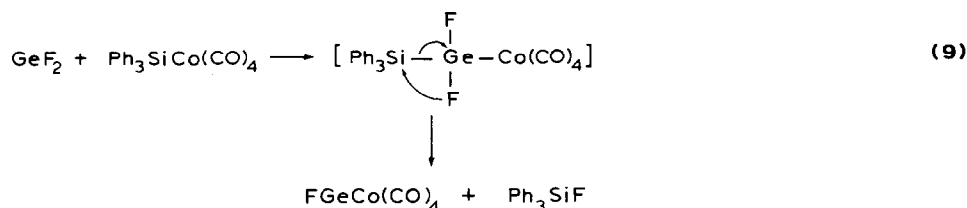
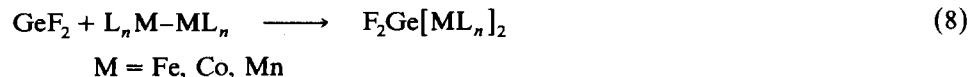
The intermediate formation of the 1,3-dithiolane-2-germylene is proved by the direct reaction of this germylene with ethanedithiol, which gives the same spirogermanium compound (eq. 7)



This reaction represents the first example of insertion of germylene into an S-H bond [17,18].



The halogermynes GeF_2 and PhGeCl react readily with some metal carbonyl dimers to give the corresponding insertion adducts, which have been isolated [20] (eq. 8).



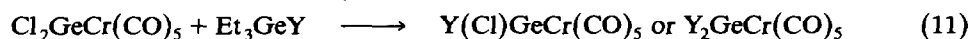
Similar insertions into group 14-transition metal bonds lead to unstable adducts that decompose by an α -elimination process to give the first germylenes with germanium-transition metal bonds (eq. 9 and 10).



These new divalent germanium species undergo specific germylene reactions. Cycloaddition with 2,3-dimethylbutadiene leads to germacyclopentene and, unusually, is thermally reversible. Insertion into the cobalt-cobalt bond of $\text{Co}_2(\text{CO})_8$ gives a polymetallated compound [20].

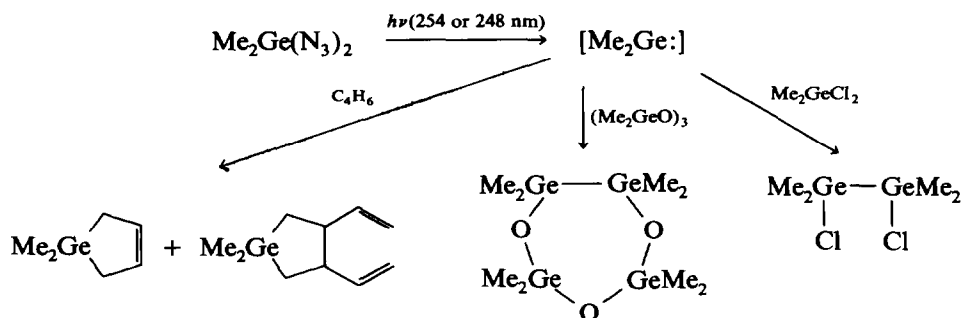
Transition metal-germylene complexes of the type $\text{X}_2\text{GeM}(\text{CO})_5 \cdot \text{THF}$ ($\text{M} = \text{Cr}, \text{W}$; $\text{X} = \text{F}, \text{Cl}$) react with nitrones [21], aldehydes, imines and oximes [22] by nucleophilic exchange at the germanium atom to form new stable adducts. Similar reactions were observed with various oxidizing agents (e.g. dimethylsulfoxide, nitrosobenzene, pyridine-*N*-oxide) [22]. The high stability of the germanium-transition metal bond in these adducts impedes their decomposition into doubly bonded germanium intermediates >Ge=Y ($\text{Y} = \text{O}, \text{NR}$) by metathesis. Adducts with imine or oxime $\text{Cl}_2\text{GeCr}(\text{CO})_5 \cdot \text{Ph}_2\text{C=NH}$ or $\text{Cl}_2\text{GeCr}(\text{CO})_5 \cdot \text{PhCH=NOH}$ have also been described [23].

New germylene complexes were prepared by exchange reactions with organogermanes Et_3GeY where $\text{Y} = \text{N}<, \text{OR}, \text{SR}$ [23] (eq. 11).



The stabilization of these complexes by self-association depends on the nature of the heteroelement Y linked to germanium [23].

UV irradiation of matrix isolated dimethyldiazidogermane $\text{Me}_2\text{Ge}(\text{N}_3)_2$ permits identification of dimethylgermylene (Me_2Ge) by its IR and UV-visible spectra. The IR spectrum of the annealed matrix shows peaks attributable to the known dimer $\text{Me}_2\text{Ge=GeMe}_2$. Chemical trapping experiments in room temperature solutions are compatible with a generation of free Me_2Ge by the irradiation of $\text{Me}_2\text{Ge}(\text{N}_3)_2$ [24] (Scheme 2).

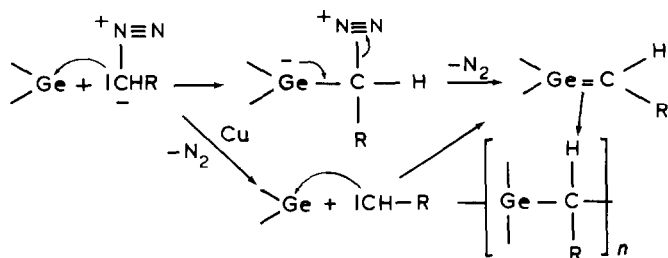


Scheme 2

Multiply-bonded germanium species

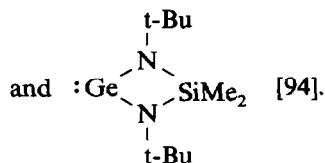
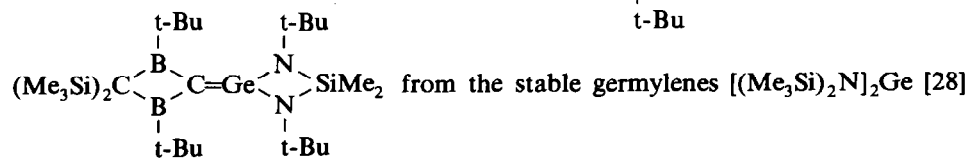
Germenes: $Ge=C$ species

Germenes containing $p\pi-p\pi$ bonds between germanium and carbon are among the most intensively investigated species in germanium chemistry. We have described a novel route to germene by a direct interaction between a germylene and diazo compounds or carbene generated in situ [25] (Scheme 3).

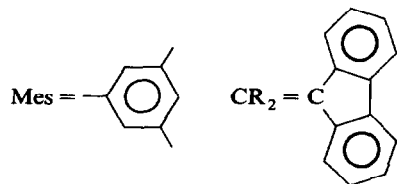
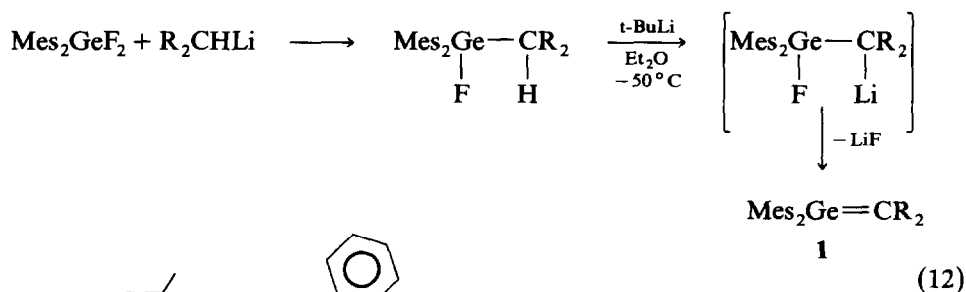


Scheme 3

A similar route to germenes was recently described by Berndt [26,27] in the synthesis of the stable germenes $(Me_3Si)_2C \begin{matrix} t-Bu \\ | \\ B \\ | \\ B \\ | \\ t-Bu \end{matrix} C=Ge[N(SiMe_3)_2]_2$ and



The stable germene **1** was prepared by dehydrofluorination of the corresponding fluorenylgermane [29,30] (eq. 12).



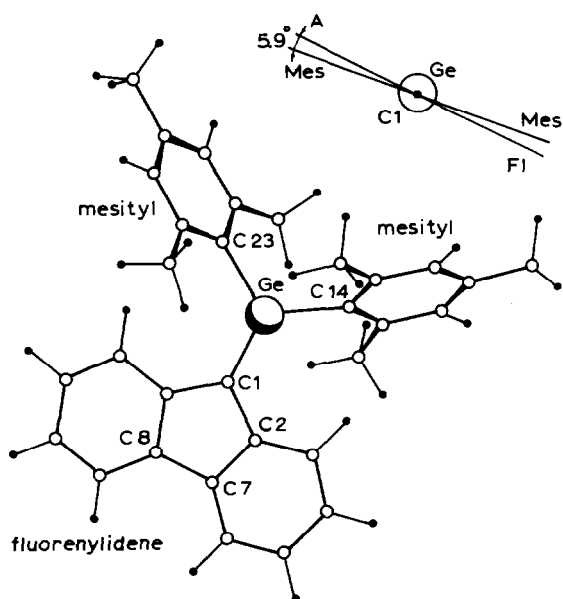


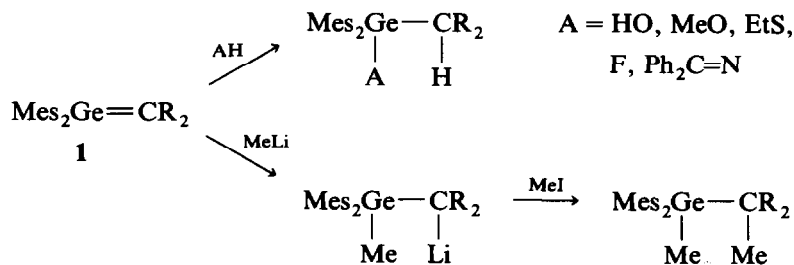
Fig. 1. ORTEP view of **1** (reprinted with permission from *Angew. Chem., Int. Ed. Engl.* 27 (1988) 828.)

Germene **1** is thermally very stable but highly air sensitive. It forms stable $\begin{matrix} \diagup \\ \text{Ge}=\text{C} \\ \diagdown \\ \text{B} \end{matrix}$ adducts with Lewis bases such as ethers or amines.

The X-ray structures of $\text{Mes}_2\text{Ge}=\text{CR}_2$ (**1**) and $\text{Mes}_2\text{Ge}(\text{H})\text{C}(\text{H})\text{R}_2$ (**2**) have been determined [30] (Fig. 1).

The $\text{Ge}=\text{C}$ double bond (1.80 Å) is about 10.5% shorter than the corresponding $\text{Ge}-\text{C}$ single bond (2.01 Å). The germanium atom is planar and the twisting around the $\text{Ge}-\text{C}$ bond is only 6° . These results are in good agreement with *ab initio* calculations which predict a planar structure for $\text{H}_2\text{Ge}=\text{CH}_2$ [31].

The germene is highly reactive toward various electrophiles and nucleophiles. For example, protic reagents AH , halogens, and lithio-compounds add very easily to the double bond (Scheme 4).

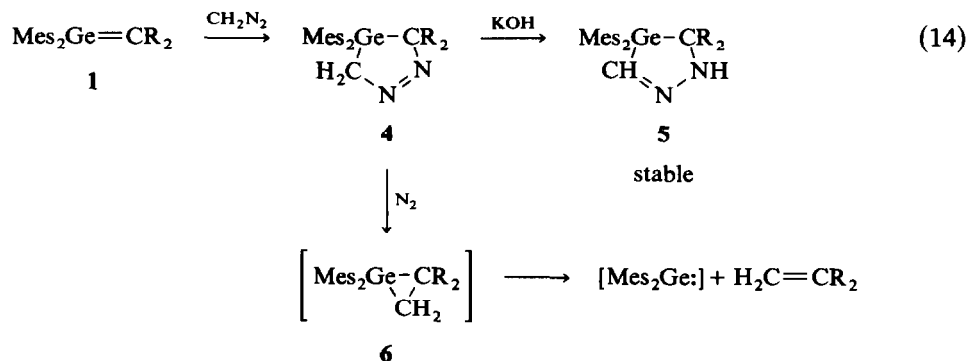


Scheme 4

It seems reasonable to postulate the formation of transient germanimine followed by dimerisation [33].

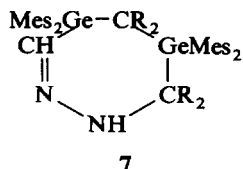
The structure of germanimine intermediate is very close to that of the germanimines obtained by Glidewell that are stabilized by greater steric hindrance at germanium (two Me_3Si) $_2\text{N}$ instead of the two mesityl groups [34].

Reaction of germene $\text{Mes}_2\text{Ge}=\text{CR}_2$, **1**, with diazomethane leads, depending on the experimental conditions, to the germapyrazolines **4** or **5**. Thermal decomposition of **4** affords an unstable germirane **6**, as evidenced by its decomposition products [3] viz., [2 + 1], 9-methylenefluorene and dimesitylgermylene [35] (eq. 14).



Krebs et al. have reported the same type of decomposition for the germapyrazolidine **4** [36].

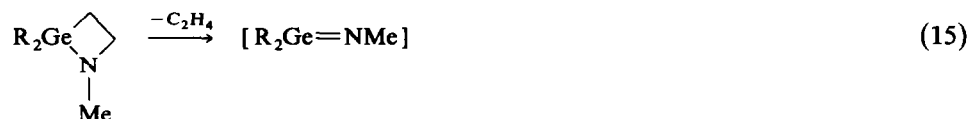
When diazomethane is added to an excess of the germene at -78°C the dipolar intermediates $\text{Mes}_2\text{GeCH}=\text{N}^+\text{NH}^- \leftrightarrow \text{Mes}_2\text{GeCH}_2\text{N}^+=\text{N}^-$ can be detected by trapping reactions with germene **1** that lead to the seven-membered ring species **7**.



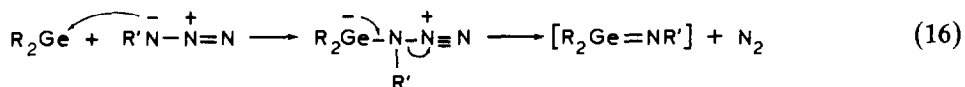
Compound **7** is very stable as a solid, but slowly decomposes in solution at room temperature to give germene **1** and germapyrazolidine **5**. Thus **7** can be considered as a store for the germene [35].

Germanimines: $\text{Ge}=\text{N}$ -species

The first generation of germanimine intermediates $\text{R}_2\text{Ge}=\text{NR}'$ involves a β -elimination from unstable germaazetidines [37,38] (eq. 15).

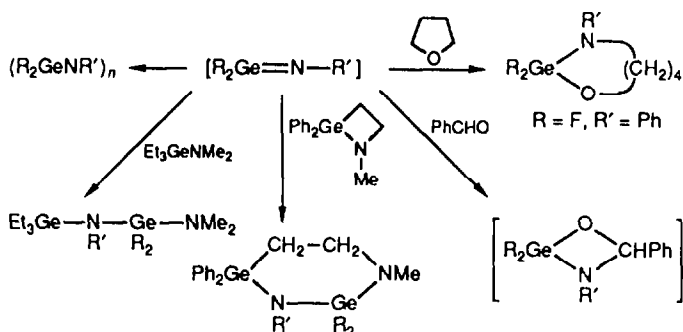


They are also formed by the action of phenyl or methyl azides on germynes [39] (eq. 16).

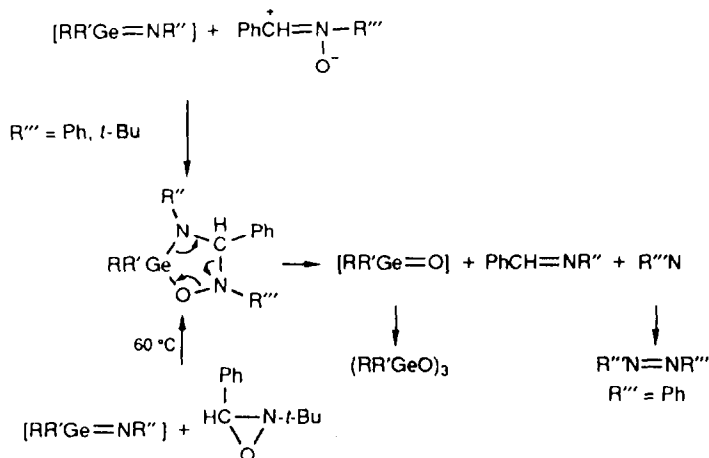


The direct interaction of a gerylene with a nitrene also leads to germanimines [40]. Like silanimines the germanimines can also be generated by photolysis of triorganogermanium azides [41]. Studies of ring opening of cyclogermazanes $(R_2GeNR')_n$ ($n = 2, 3$) [42,43] and chlorocyclotrigermazanes $(Cl_2GeNR)_n$ ($n = 2, 3$) [44] induced by Lewis bases (Et_3N , HMPA) or Lewis acid ($ZnCl_2$, $M(CO)_6$, $M(CO)_5$, THF ($M = Cr, W$)) show the existence of an equilibrium between cyclogermazanes and germanimines. The 1,3-cycloaddition with nitrones is regarded as chemical evidence for germanimine formation in this equilibrium [42–44].

Transient germanimines are characterized in the form of polygermazanes, by insertion into the germanium-nitrogen bond of gerylazetidine and dimethyl(trieth-



Scheme 6



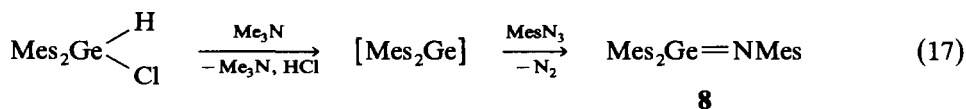
Scheme 7

ylgermyl)amine and by insertion into a tetrahydrofuran ring and formation of a seven membered heterocycle as well as by a pseudo Wittig reaction with benzaldehyde to form the unstable germaoxazetidine [37-39] (Scheme 6)

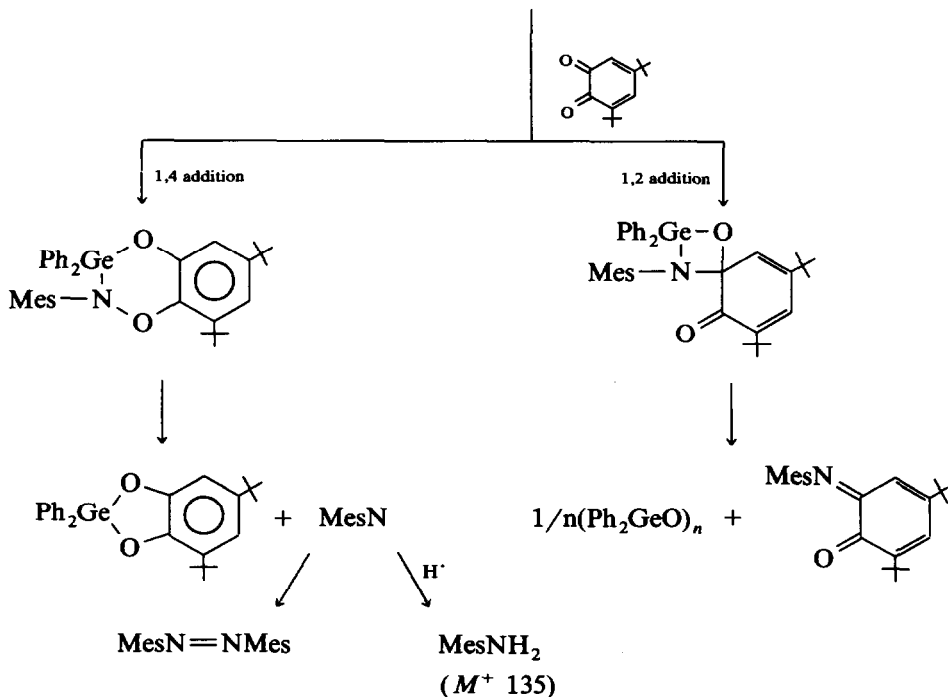
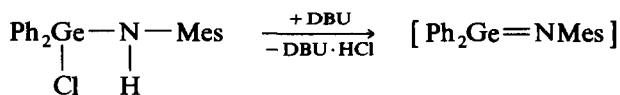
The [2 + 3] cycloadditions of germanimines $RR'Ge=NR''$ ($R=Ph$; $R' = Ph, Cl$; $R'' = Me, Ph, t-Bu$) with nitrones (diphenyl or phenyl-tert-butyl nitron) as well as their insertion reactions on oxaziridines lead to germanones ($RR'Ge=O$) imines $PhCH=NR''$ and nitrenes, probably via transient 2-germa-1-oxa-3,5-diazolidines. The imines formed contain the NR'' group of the initial germanimines [42,43] (Scheme 7).

The transient diphenyl-*N*-mesitylgermanimine ($Ph_2Ge=NMe$) (from dehydrohalogenation of $Ph_2ClGeNHMe$ by DBU) gives unstable 1,4-adducts and 1,2-adducts with 3,5-di-tert-butylorthoquinone [45] (Scheme 8)

Trimesitylgermanimine ($Mes_2Ge=NMe$) **8** was obtained from the reaction between dimesitylgermylene and mesitylazide [46,67] (eq. 17) and also by photolysis

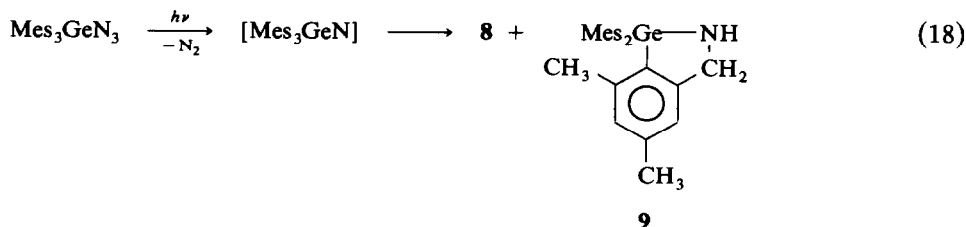


of trimesitylgermyl azide, involving the transitory formation of trimesitylgermylnitrene and a Curtius-like rearrangement.



Scheme 8

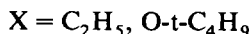
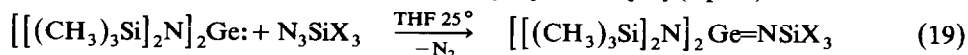
The cyclic isomer **9** is also formed by insertion of germylnitrene into the C–H bond of the mesityl group [46,47] (eq. 18).



Compound **8** was characterized by pseudo Wittig reaction with benzaldehyde and formation of $\text{PhCH}=\text{NMes}$ and $(\text{Mes}_2\text{GeO})_2$ [47]. Cycloaddition [2 + 3] with diphenylnitrene also takes place. In the presence of trimethylamine $\text{Mes}_2\text{Ge}=\text{NMes}$ behaves like a monomer, which is probably stabilized in solution by association with the nucleophile [47].

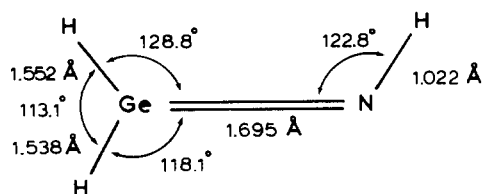
Recently Ando et al. have characterized the same trimesitylgermanimine **8** in a 3-methylpentane matrix at 77 K. The formation of azagermacyclopentane **9** is also observed [48]. $\text{Mes}_2\text{Ge}=\text{NMes}$ is intensely yellow, with absorption maxima at 309 and 459 nm.

The reactions between germylene and azides already described [39] permit the isolation of two stable germanimines **10**, **11** from bis[bis(trimethylsilyl)amino]germylene and triethylsilylazide or tri-tert-butoxysilyl-azide [49] (eq. 19).



10 **11**

Germanimine ($\text{H}_2\text{Ge}=\text{NH}$) is predicted to be planar. Its optimized geometry at the SCF level is shown in Scheme 9 [31]. The $\text{Ge}=\text{N}$ bond length (1.695 Å) is shorter than a normal $\text{Ge}-\text{N}\sigma$ bond (1.83–1.87 Å) [49,50].

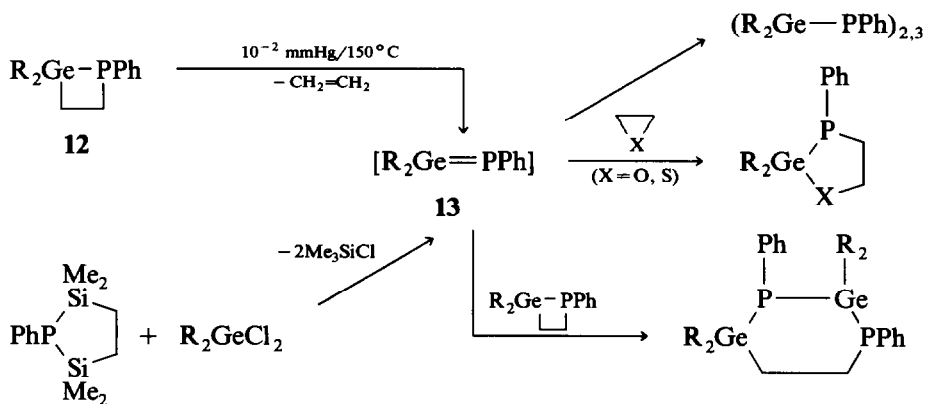


Scheme 9

The germylene $\text{HGe}=\text{NH}_2$ is calculated to be more stable than the doubly bonded isomer $\text{H}_2\text{Ge}=\text{NH}$. The energy difference between HGeNH_2 and $\text{H}_2\text{Ge}=\text{NH}$ is 32 kcal/mole [31].

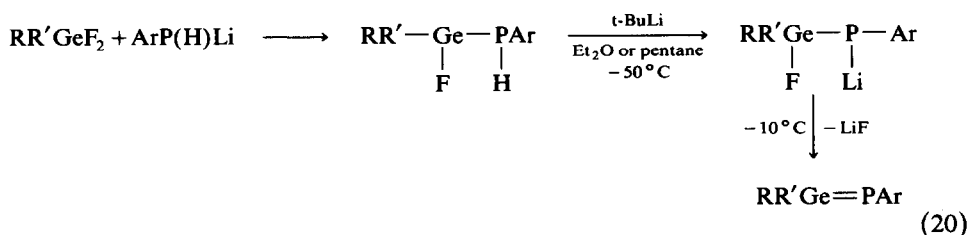
Germaphosphenes Ge=P-species

Until recently, germaphosphenes $\text{RR}'\text{Ge}=\text{PR}''$ were postulated only as reactive intermediates and characterised by trapping reactions. They were obtained by two routes, namely thermal decomposition of 2-germaphosphetanes **12** and dechlorosilylation between dialkyldichlorogermenes and disilylphosphines. The transient germaphosphenes **13** were clearly characterized by formation of dimeric or trimeric cyclic germylphosphines and by insertion and ring expansion reactions with oxirane, thiirane and 2-germaphosphetanes [51–53] (Scheme 10)

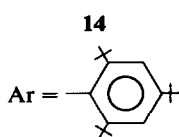


Scheme 10

Sila- and stanna-phosphenes $\text{R}_2\text{M}=\text{PR}$ ($\text{M} = \text{Si}$) [53,54]; $\text{M} = \text{Sn}$ [53,55] can be formed and characterised similarly. Use of substituents having strong steric and electronic effects has recently allowed isolation of three stable germaphosphenes **14**, **15**, **16** [56,57]. The best route to stable germaphosphenes involves the dehydrofluorination of the corresponding fluorogermylphosphines by tert-butyllithium at low temperature (eq. 20).



$\text{R}, \text{R}' = \text{Mes}$ [56], $\text{Mes}, t\text{-Bu}$ [57], $t\text{-Bu}$ [57]



In the case of $\text{Mes}(t\text{-Bu})\text{Ge}=\text{PAr}$ **15**, the formation of stereoisomer $\begin{array}{c} \text{Mes} \\ \diagdown \\ \text{Ge}=\text{P}-\text{Ar} \\ \diagup \\ t\text{-Bu} \end{array}$, **15a** is only observed in reactions at low temperature. After 5 h at room temperature complete isomerisation is observed, with formation of $\begin{array}{c} t\text{-Bu} \\ \diagdown \\ \text{Ge}=\text{P}-\text{Ar} \\ \diagup \\ \text{Mes} \end{array}$, **15b**.

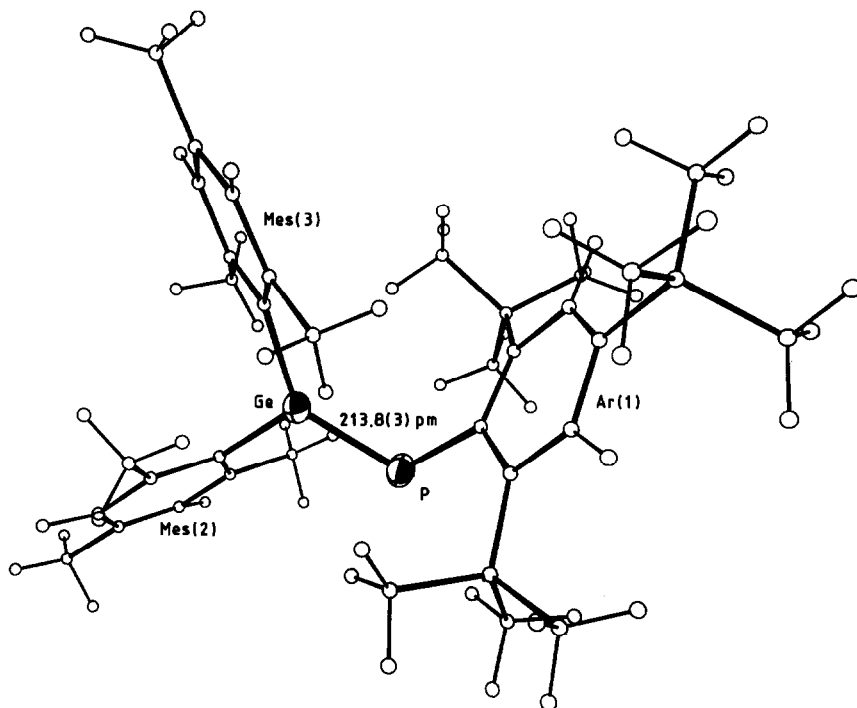


Fig. 2. ORTEP view of **14** (reprinted with permission from *Organometallics* 7 (1988) 1010).

The structure of **15b** has been determined by an X-ray study [57]. The *cis-trans* isomerization barrier (22.3 kcal/mole) has been determined by NMR spectroscopy. The stable germaphosphenes form yellow-orange crystals and air and moisture sensitive but thermally very stable (up to 150°C). They can be stored without change for months in an inert atmosphere. Germaphosphenes are thermochromic,

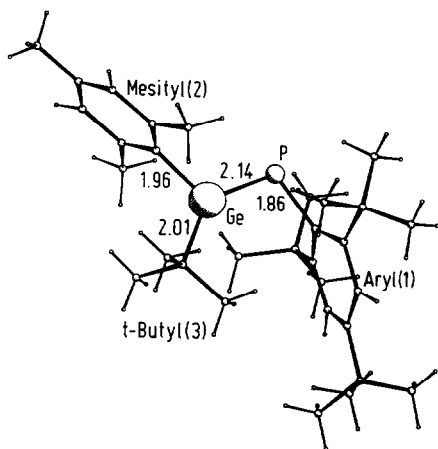
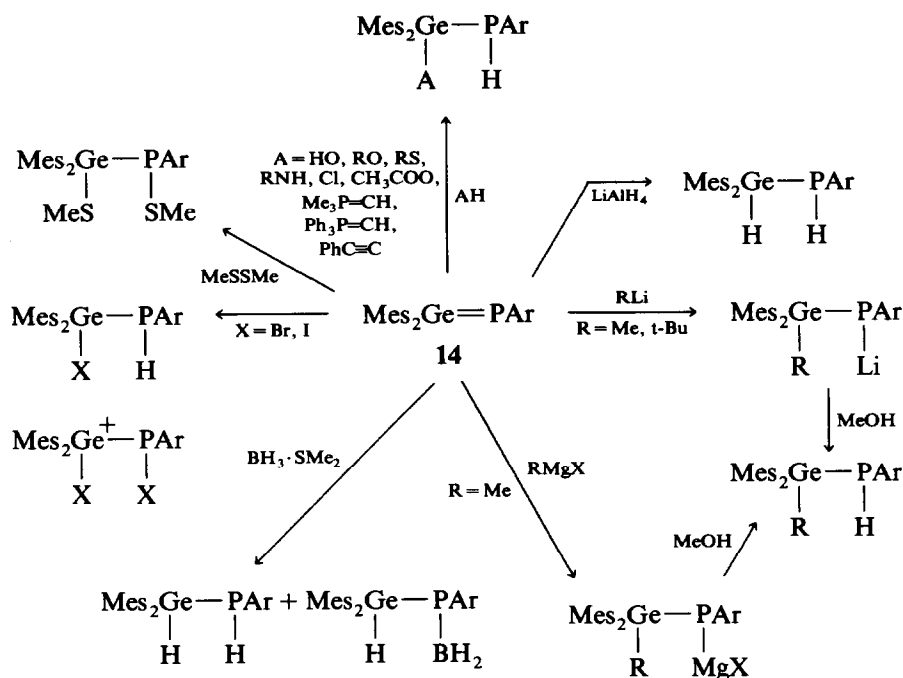


Fig. 3. ORTEP view of **15b** (reprinted with permission from *New J. Chem.* 13 (1989) 389)



Scheme 11

they are yellow at -80°C , orange at room temperature, and orange-red at 180°C . The ^{31}P NMR chemical shifts (148.5–178.2) are characteristic of dicoordinated phosphorus. The structures of $\text{Mes}_2\text{Ge}=\text{PAR}$, **14**, and $\text{Mes} \begin{array}{l} \diagdown \\ \text{Ge}=\text{P}-\text{Ar} \\ \diagup \\ \text{t-Bu} \end{array}$, **15b**, have

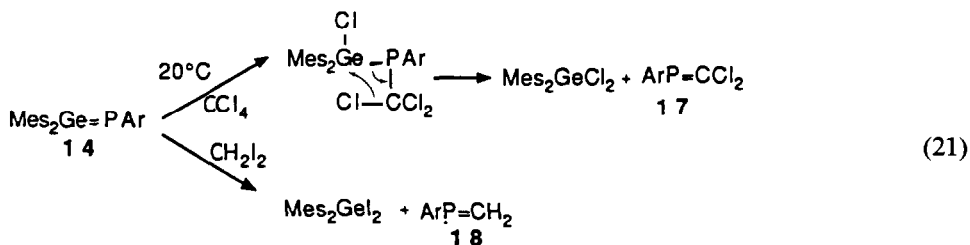
been determined by X-ray crystallography [57,58] (Figs. 2 and 3). In each case the germanium–phosphorus double bond length (2.138 and 2.144 Å) is significantly shorter than the standard germanium–phosphorus single bond (2.33–2.35 Å) [59–62]. This rather important shortening (about 8.5%) and the essentially planar double bond geometry support the existence of a true germanium–phosphorus double bond. Raman emission of the Ge=P bond is at 503 cm^{-1} for $\text{Mes}_2\text{Ge}=\text{PAR}$, **14**, and 501.5 cm^{-1} for $\text{Mes} \begin{array}{l} \diagdown \\ \text{Ge}=\text{P}-\text{Ar} \\ \diagup \\ \text{t-Bu} \end{array}$, **15b** [41]

Germaphosphene **14** is very reactive towards compounds containing active hydrogen, such as water, alcohols, thiols, amines, mineral and organic acids, phosphorus ylides, and acetylene compounds [53,56,63,64] (Scheme 11). These additions are highly regiospecific, leading to only secondary phosphines.

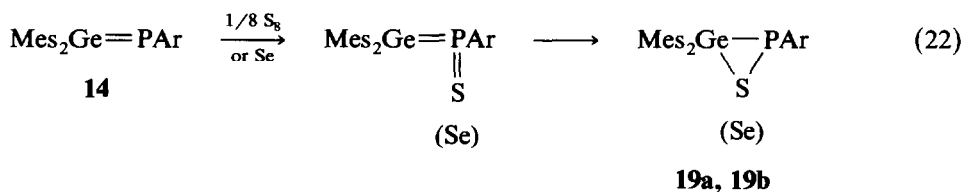
Bromine and iodine react to give the expected adduct and the halogermaphosphine, probably via a radical process and intermediate formation of $\text{Mes}_2\text{Ge}(\text{X})\text{PAR}$ [63,64]. Nucleophiles such as lithium compounds or Grignard reagents add readily to the double bond. Reduction of the germanium–phosphorus bond is observed with lithium aluminium hydride and borane, together with formation of the adduct in the latter case.

Germaphosphene **14** reacts with dimethyl disulfide by a radical process [63,64].

Reactions of **14** with organic halogenated compounds such as carbon tetrachloride or diiodomethane lead to phosphalkenes **17**, **18** [63,64] (eq. 21).



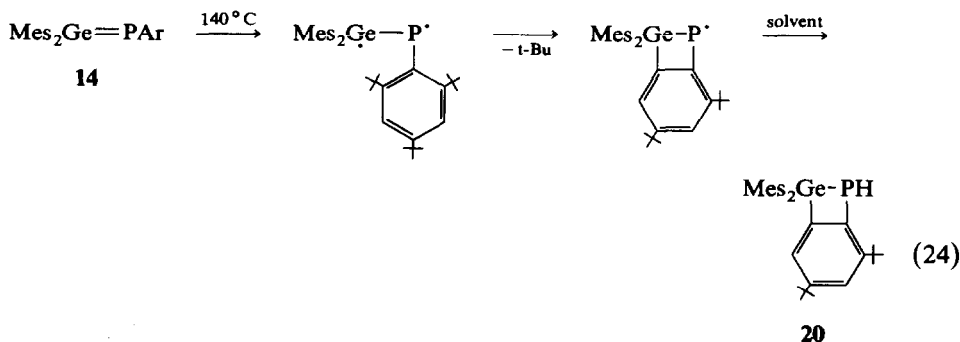
Cycloadditions of sulfur or selenium leading to three-membered rings **19a**, **19b** [63] (eq. 22) have also been observed.



The X-ray structure of germaphosphathirane suggests that the structure may be intermediate between a normal three-membered ring and π -complex [59] (eq. 23).

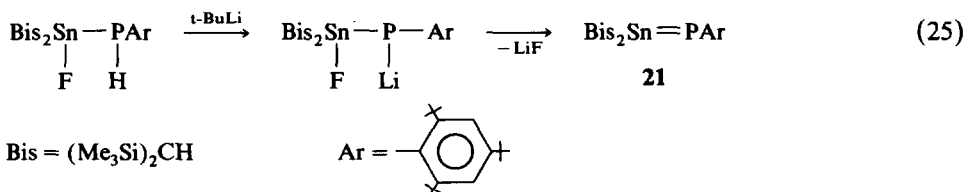


Thermolysis of **14** affords in near quantitative yield a stable germaphosphetene **20** [62]. An X-ray study shows it to be a nearly planar four-membered heterocycle. The formation of germaphosphetene **20** may be accounted for in terms of a radical process involving intramolecular radical aromatic substitution followed by hydrogen abstraction from the solvent [62] (eq. 24).



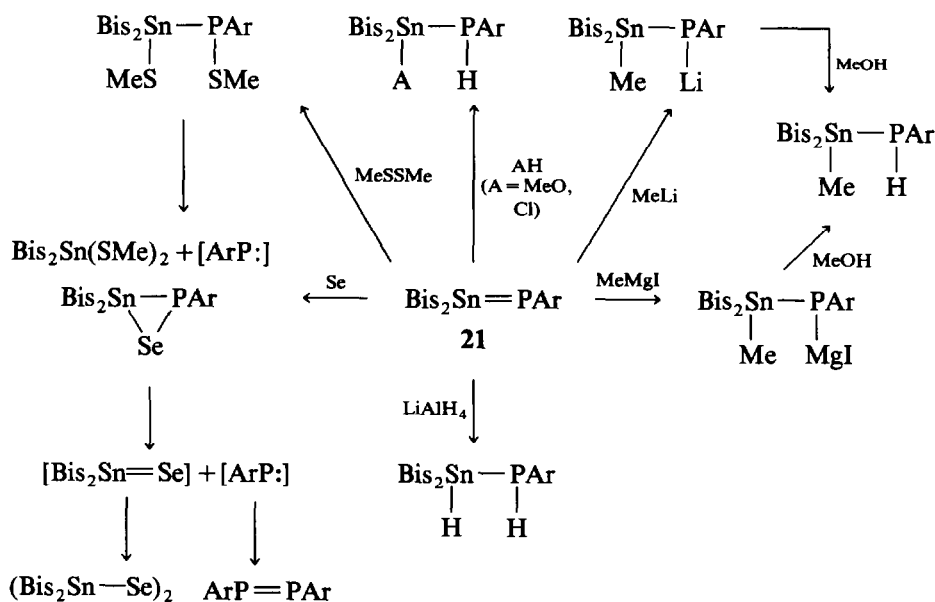
We have also studied stannaphosphene compounds. Only one stable stannaphosphene $\text{R}_2\text{Sn}=\text{PAr}$, **21**, has been isolated as a monomer [65]. This compound

was synthesized by dehydrofluorination of the corresponding fluorostannylphosphine with tert-butyllithium (eq. 25).



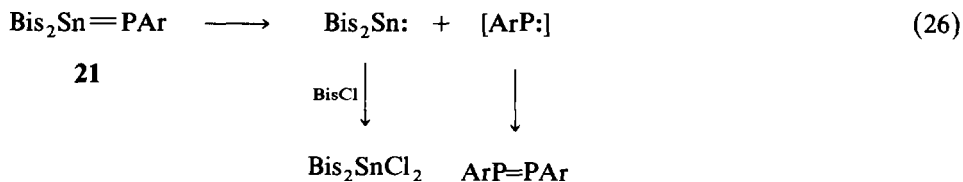
The stannaphosphene structure was unambiguously demonstrated by NMR spectroscopy. The ^{31}P NMR chemical shift (+204.7 ppm) falls in the range of sila and germaphosphenes. The ^{119}Sn chemical shift at very low field (+658.3 ppm/ Me_4Sn) is normal for a tricoordinate $p\pi$ -hybridized tin. Very significant are the coupling constants between phosphorus and tin $^1J(\text{P}-^{117}\text{Sn}) = 2191$ $^1J(\text{P}-^{119}\text{Sn}) = 2195$ Hz. These values are much larger than those for single-bonded tin and phosphorus compounds (1150–1200 Hz) [65]. A similar effect has been observed for $^1J(\text{P}-^{29}\text{Si})$ in silaphosphenes [66]. The structure of stannaphosphene was corroborated by its chemical behaviour: additions of protic reagents (alcohols, HCl), organolithium compounds, and Grignard reagents to the double bond are regioselective and confirm the expected polarity $\delta^+\text{Sn}=\text{P}\delta^-$. Reduction of the double bond by LiAlH_4 , addition of dimethyl disulfide, and cycloaddition with selenium are also observed [64,65,67] (Scheme 12).

Thermolysis of stannaphosphene in a sealed tube at 70°C for 15 h gives a



Scheme 12

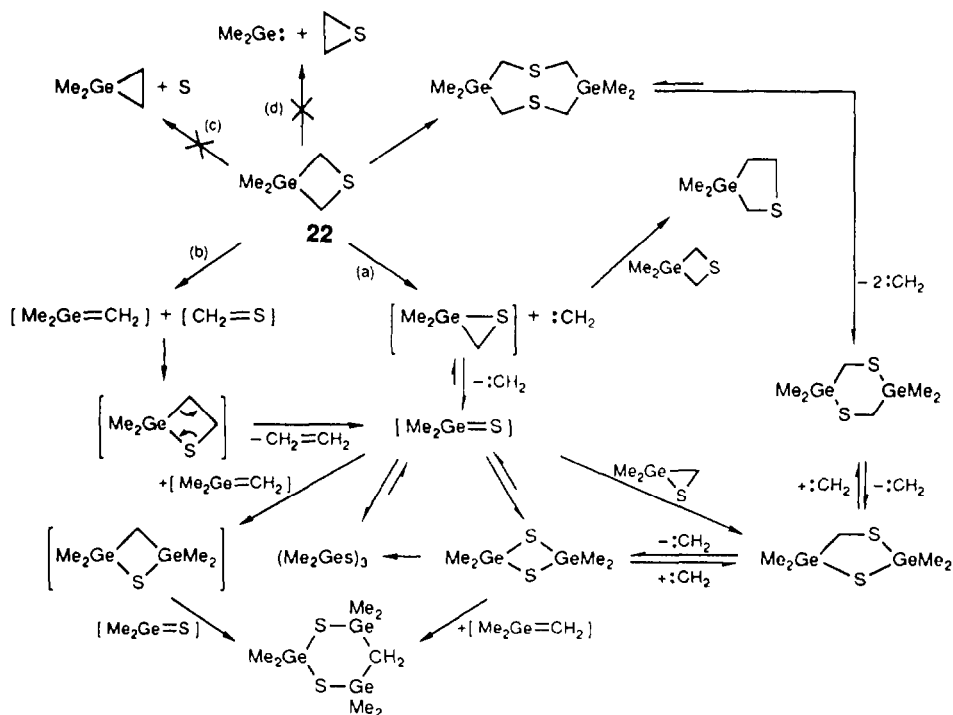
completely different reaction from that observed in the case of germaphosphenes. It leads to the stannylene and the phosphinidene [64,67] (eq. 26).



Germanones and germathiones: Ge=X (X = O, S) species

Reactions of germynes with oxygen or sulfur donors is a direct interaction which leads to germanones or germathiones. O₂, KMnO₄, DMSO, C₅H₅NO and S₈ were the oxidizing reagents [1]. A similar reaction was described recently by DuMont in the reaction between elemental sulfur and bis(2,4,6-tri-*t*-butylphenyl)germylene, which gave a germaindanethiol, via the intermediate germanethione, by addition of an *ortho-t*-butyl group C–H bond to the Ge=S double bond [68].

Various germa-oxetanes and -thietanes are thermally unstable and lead, probably via a β -elimination process, to transient dialkylgermanones and germathiones, which can be trapped with oxirane or thirane [1]. Thermolysis, pyrolysis, and photolysis of thiagermetane Me₂GeCH₂SCH₂, **22**, and dithiagermolane Me₃GeCH₂SSCH₂, **23**, give various new germylated heterocycles [69,70]. Decom-



Scheme 13

position of thiagermetane, **22**, probably proceeds by two competitive mechanisms involving transient germene [$\text{Me}_2\text{Ge}=\text{CH}_2$] and germanethione ($\text{Me}_2\text{Ge}=\text{S}$), thiagermirane $\text{Me}_2\text{GeCH}_2\text{S}$, and thiadigermetane $\text{Me}_2\text{GeCH}_2\text{Ge}(\text{Me}_2)\text{S}$ (Scheme 13).

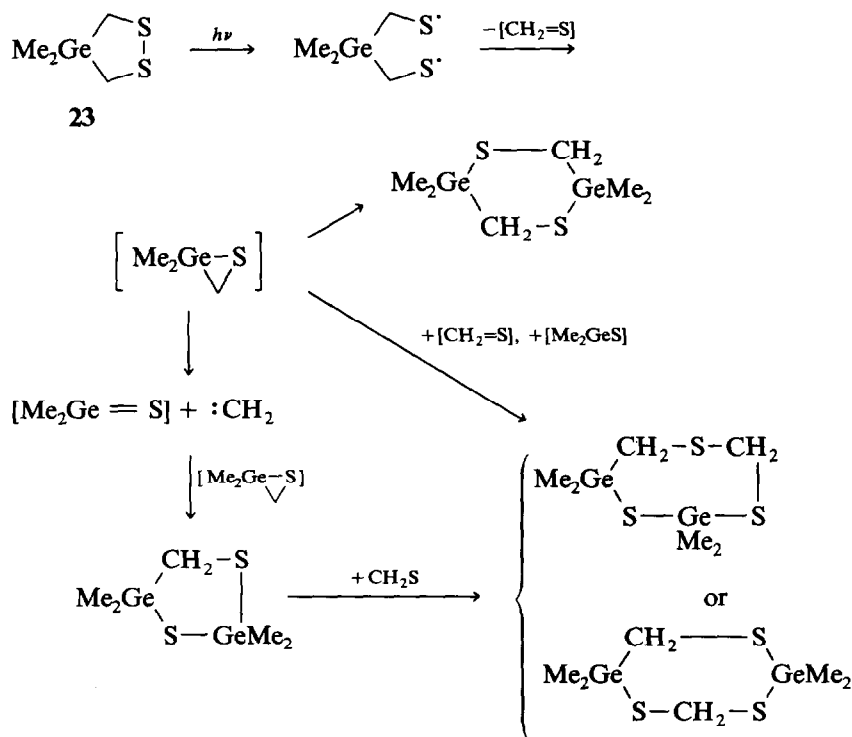
These results indicate the possible occurrence of [2 + 2] cycloaddition between dimethylgermene and dimethylgermanethione.

The photolysis of dithiagermolane $\text{Me}_2\text{GeCH}_2\text{SSCH}_2$, **23**, is outlined in Scheme 14.

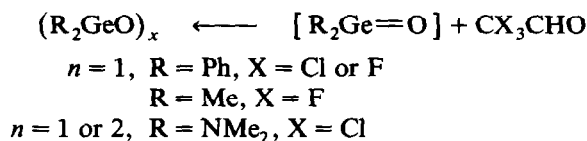
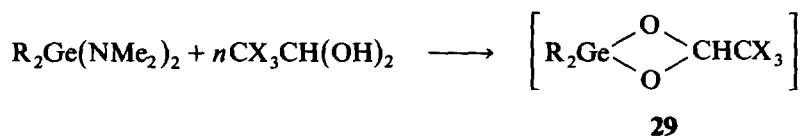
Pyrolysis of the thiagermetane dioxide $\text{Me}_2\text{Ge}-\text{CH}_2\text{S}(\text{O}_2)\text{CH}_2$ is also postulated to involve multiply-bonded germanium species, namely the germene $\text{Me}_2\text{Ge}=\text{CH}_2$ and probably a novel doubly-bonded germanium species, the germasulfene $\text{Me}_2\text{Ge}=\text{SO}_2$, detected in the mass spectrum of the four-membered-ring thiagermetane dioxide [70]. Another interesting precursor for dimethylgermanethione and dimethylgermene is the 2,4-digermathiane $\text{Me}_2\text{GeCH}_2\text{Ge}(\text{Me}_2)\text{S}$ [71].

Similar decompositions of thia- or oxa-digermetane intermediates are postulated in investigations of the action of S_8 or O_2 on the tetra-germadimercurocane [72] or on the [bis(dimethylgermyl)alkane]iron tetracarbonyl [73], which in a first step give the relatively stable dithia- or dioxo-digermolanes [72,73].

The phosphorylated heterocycle $\text{Me}_2\text{GeSP}(\text{S})(\text{An})\text{S}$, **24** (An = anisyl), stable at room temperature, gives the transient species (AnPS_2) and $(\text{Me}_2\text{Ge}=\text{S})$ [74]. The evidence for this is the formation of the expected thiirane adducts of the germanethione and of (AnPS_2) when thiirane is present in the reaction mixture (eq. 27).

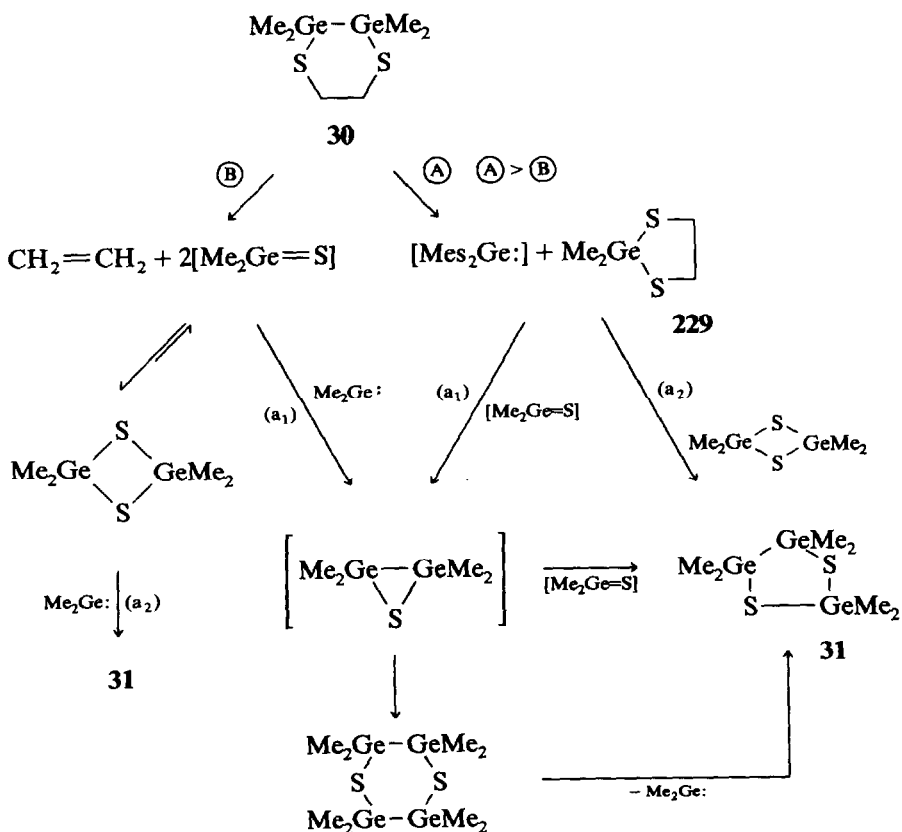


Scheme 14



Scheme 17

The germathiaphosphirane $\text{Mes}_2\text{Ge}-\text{PAr}$, **25**, when heated with an excess of sulfur gives the metadithiophosphonate, **26**, and the 2,4-digerma-1,3-dithietane **27**. Three possible routes involving formation of dimesitylgermatione by decomposition of three- or four-membered heterocycles have been suggested to be involved in formation of the products [59] (Scheme 15).



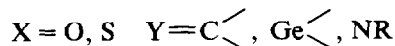
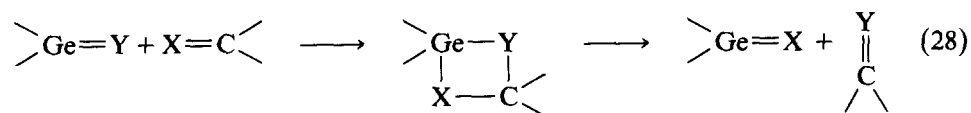
Scheme 18

An interesting precursor to dimethylgermanone is the 1,3,2-dioxagermetane, **28**, which is stable at room temperature (in associated dimer form). Dilution or low pressures induce decomposition to form chloral and dimethylgermanone by β -elimination. Dimethylgermanone is readily trapped by ethylene oxide or thiirane [75] (Scheme 16).

Similar decomposition of various dioxagermetane **29** intermediates has been suggested [75] (Scheme 17).

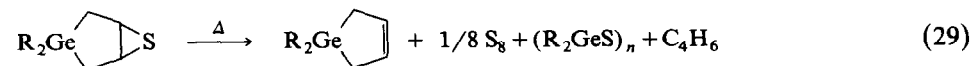
Dimethylgermanethione and dimethylgermylene are probably formed in the thermolysis of the 2,3-digerma-1,4-dithiane, **30**, which leads to stable germylated heterocycles. The authors suggest two concurrent decomposition mechanisms A and B [76] (Scheme 18)

Germanones and germathiones have been often suggested as intermediates formed in pseudo-Wittig reactions of germene [1,77,78] digermenes [79] and germanimines [37-39,42] (eq. 28).



Direct generation of the dimethylgermanone from thermolysis in a flow system of the 6-oxa-3-germabicyclo[3,1,0]hexane, **32**, via a transient 2-germaoxetane has also been suggested [80,81] (Scheme 19).

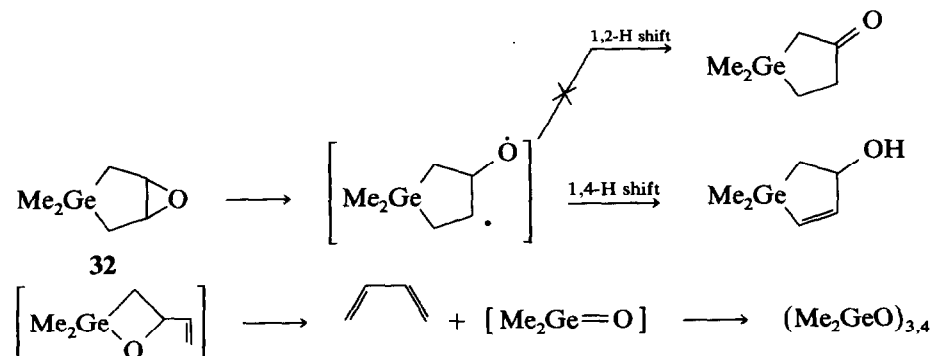
Similarly, thiiranes **33** are unstable and potential precursors of germathiones [82] (eq. 29).



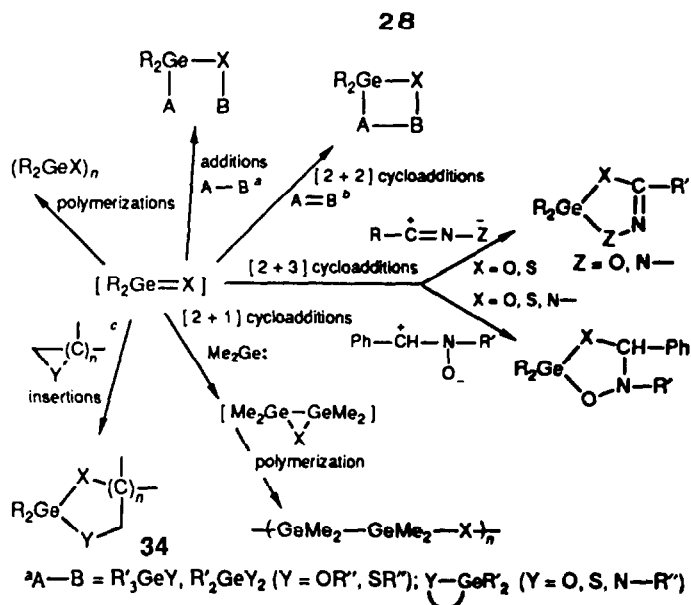
33

R = Me, Ph

Cyclogermathianes $(\text{R}_2\text{GeS})_3$ very easily give the germanethione $(\text{R}_2\text{Ge}=\text{S})$ by thermal and catalytic dissociation. Basic solvents such as Et_3N or HMPA and catalysts as $(\text{Ph}_3\text{P})_2\text{PdCl}_2$ induce these dissociations, and catalyze the reaction of



Scheme 19



Scheme 20

germanethiones with three- and four-membered rings [83]. Thermolysis of $(Me_2GeS)_3$ has been found to be useful for the production of matrix-isolated germathione [84].

Germanones are also postulated as intermediates in the thermal dissociation of various germoxanes [75,83].

It should be noted that the first isolable compound with an intramolecular base stabilized $Ge=S$ double bond was recently reported. This compound was obtained by sulfurization of a cyclic bis(amino)germylene [85]. The oxidation product of the same germylene is a dimer of the corresponding germanone [85].

Germanones and germathiones, with their strongly polarized bonds, are highly reactive; types of reactions characteristic of these species are polymerisation or oligomerisation, addition to various σ bonds of acyclic or cyclic organometallic compounds, insertion and expansion reactions with strained organic heterocycles, and [2 + 1], [2 + 2] and [2 + 3] cycloaddition reactions [1,83,86–88] (Scheme 20).

Many insertions of germanones and germathiones into σ bonds $Ge-Y$ ($Y = O, S, N, P$, etc.) have been described [1,69–71,74]. Insertions of dimethylgermanone into $Si-O$ and $Si-Cl$ bonds are also observed [81]. Insertion into a $C-H$ bond from the *ortho*-*t*-butyl group of germanethione intermediate has also been postulated [68].

Dialkylgermanones and dialkylgermanethiones react with three- or four-membered ring species to give the corresponding germaheterocycles 34 [83,86]. The

terms of a decomposition of the trimer and the presence 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 9.95; 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 [90-92].

The spectrum of the products of the decomposition of $\text{Me}_2\overline{\text{GeOCH}(\text{CCl}_3)\overline{\text{O}}}$ includes the bands characteristic of the chloral and of the dimethylgermanone, whose ionization potentials are 9.7 (n_0) 10.2 ($\pi\text{Ge}=\text{O}$) 11.0 ($\sigma\text{Ge}-\text{O}$) and 12.1 eV ($\sigma\text{Ge}-\text{C}$) [92,93].

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

Recently the IR spectrum of the matrix-isolated dimethylgermathione obtained by gas phase pyrolysis of $(\text{Me}_2\text{GeS})_3$ was reported [84]. The same IR spectrum is obtained from the product of interaction between atomic sulfur and dimethylgermylene obtained by photodecomposition of $\text{O}=\text{C}=\text{S}$ and $\text{Me}_2\text{Ge}(\text{N}_3)_2$, respectively [84].

In conclusion it appears that progress in the field on multiply-bonded germanium species has been very important during the ten past years. The first stable germenenes, digermenenes (3), germaphosphenes, germanimines and germathiones have recently been isolated. These new "organometallic functions" $\text{>Ge}=\text{Y}$ ($\text{Y}=\text{C}<$, $\text{N}<$, $\text{P}<$, O , S , $\text{Ge}<$) are much more reactive than their carbon analogues, and are the precursors to many new compounds and structures in organogermanium chemistry. These unsaturated species could be useful precursors of new high performance materials of practical interest, such as polymers, conductors, ceramics, etc..

The field of new compounds and intermediates containing *sp*-hybridized germanium, such as $-\text{Ge}\equiv\text{X}$, $\text{Y}=\text{Ge}=\text{Y}$, at present provides the most promising challenge in organogermanium chemistry.

References

- 1 J. Satgé, *Adv. Organomet. Chem.*, 21 (1982) 241; *Pure Appl. Chem.*, 56 (1984) 137; *Rev. Silicon Germanium Tin Lead Compd.*, 8 (1986) 291; *Bull. Soc. Chim. Belg.*, 91 (1982) 1019.
- 2 P. Rivière, M. Rivière-Baudet, J. Satgé, in G. Wilkinson, F.G.A. Stone and E.W. Abel (Eds.), *Comprehensive Organometallic Chemistry*, Vol. 2, Pergamon Press, New York, 1982, Chap. 10, p. 399.
- 3 J. Barrau, J. Escudié, J. Satgé, *Chem. Rev.*, 90 (1990), 283.
- 4 W.P. Neumann, *Nachr. Chem. Tech. Lab.*, 30 (1982) 190.
- 5 M.F. Lappert, *Rev. Silicon Germanium Tin Lead Compd.*, 9 (1986) 129.
- 6 W. Petz, *Chem. Rev.*, 86 (1986) 1019.
- 7 R. West, *Science*, 225 (1984) 1109; *idem*, *Angew. Chem. Int. Ed. Engl.*, 26 (1987) 1201.
- 8 A.G. Brook, K.M. Baines, *Adv. Organomet. Chem.*, 25 (1986) 1.
- 9 G. Raabe, J. Michl, *Chem. Rev.*, 85 (1985) 419; S. Patai and Z. Rappoport (Eds.), *The Chemistry of Organic Silicon Compounds*, Vol. 2, Wiley, Chichester, 1989, p. 1015.
- 10 N. Wiberg, *J. Organomet. Chem.*, 273 (1984) 141.
- 11 A.H. Cowley, N.C. Norman, *Prog. Inorg. Chem.*, 34 (1986) 1.
- 12 P. Rivière, A. Castel, J. Satgé, D. Guyot, *J. Organomet. Chem.*, 264 (1984) 193.
- 13 P. Rivière, A. Castel, D. Guyot, J. Satgé, *J. Organomet. Chem.*, 290 (1985) C15.
- 14 P. Rivière, A. Castel, J. Satgé, D. Guyot, *J. Organomet. Chem.*, 315 (1986) 157.
- 15 E. Michels, W.P. Neumann, *Tetrahedron Lett.*, 27 (1986) 2455.

- 16 M. Onyszczuk, A. Castel, P. Rivière, J. Satgé, *J. Organomet. Chem.*, 317 (1986) C35.
- 17 H. Lavayssière, G. Dousse, *J. Organomet. Chem.* 297 (1985) C17.
- 18 H. Lavayssière, G. Dousse, J. Satgé, *Recl. Trav. Chem. Pays-Bas*, 107 (1988) 440.
- 19 H. Lavayssière, G. Dousse, J. Satgé, Phosphorus, Sulfur, Silicon and Relat. Elem., 53 (1990) 411.
- 20 A. Castel, P. Rivière, J. Satgé, J. Moreau, R. Corriu, *Organometallics*, 2 (1983) 1498.
- 21 A. Castel, P. Rivière, J. Satgé, M. Ahbala, *J. Organomet. Chem.*, 307 (1986) 205.
- 22 A. Castel, P. Rivière, J. Satgé, M. Ahbala, *J. Organomet. Chem.*, 328 (1987) 123.
- 23 A. Castel, P. Rivière, J. Satgé, M. Ahbala, *J. Organomet. Chem.*, 331 (1987) 11.
- 24 J. Barrau, D.L. Bean, K.M. Welsh, R. West, J. Michl, *Organometallics*, 8 (1989) 2606.
- 25 P. Rivière, A. Castel, J. Satgé, *J. Am. Chem. Soc.*, 102 (1980) 541.
- 26 H. Meyer, G. Baum, W. Massa, A. Berndt, *Angew. Chem. Int. Ed. Engl.*, 26 (1987) 798.
- 27 A. Berndt, H. Meyer, G. Baum, W. Massa, S. Berger, *Pure Appl. Chem.*, 59 (1987) 1011.
- 28 M.J.S. Gynane, D.H. Harris, M.F. Lappert, P.P. Power, P. Rivière, M. Rivière-Baudet, *J. Chem. Soc., Dalton Trans.*, (1977) 2004.
- 29 C. Couret, J. Escudié, J. Satgé, M. Lazraq, *J. Am. Chem. Soc.*, 109 (1987) 4411.
- 30 M. Lazraq, J. Escudié, C. Couret, J. Satgé, M. Dräger, R.A. Dammel, *Angew. Chem. Int. Ed. Engl.*, 27 (1988) 828.
- 31 G. Trinquier, J.C. Barthelat, J. Satgé, *J. Am. Chem. Soc.*, 104 (1982) 5931.
- 32 M. Lazraq, Thesis, Toulouse University, 1988.
- 33 M. Lazraq, C. Couret, J.P. Declercq, A. Dubourg, J. Escudié, M. Rivière-Baudet, *Organometallics*, 9 (1990) 845.
- 34 C. Glidewell, D. Lloyd, K.W. Lombard, J.S. McKennie, *Tetrahedron Lett.*, 28 (1987) 343; *idem*, *J. Chem. Soc., Dalton Trans.* (1987) 2981; *idem*, *J. Chem. Soc., Dalton Trans.* (1987) 501.
- 35 M. Lazraq, J. Escudié, C. Couret, J. Satgé, M. Soufiaoui, *J. Organomet. Chem.*, 397 (1990) 1.
- 36 M.P. Egorov, S.P. Kolesnikov, O.M. Nefedov, A. Krebs, *J. Organomet. Chem.*, 375 (1989) C5.
- 37 M. Rivière-Baudet, P. Rivière, J. Satgé, G. Lacrampe, *Recl. Trav. Chem. Pays-Bas*, 98 (1979) 42.
- 38 M. Rivière-Baudet, P. Rivière, J. Satgé, *J. Organomet. Chem.*, 154 (1978) C23.
- 39 P. Rivière, A. Cazes, A. Castel, M. Rivière-Baudet, J. Satgé, *J. Organomet. Chem.*, 155 (1978) C58.
- 40 P. Rivière, J. Satgé, A. Castel, A. Cazes, *J. Organomet. Chem.*, 177 (1989) 171.
- 41 G. Bertrand, J.P. Majoral, A. Bacereido, *Acc. Chem. Res.*, 19 (1986) 17.
- 42 G. Lacrampe, H. Lavayssière, M. Rivière-Baudet, J. Satgé, *Recl. Trav. Chem. Pays-Bas*, 102 (1983) 21.
- 43 M. Rivière-Baudet, P. Rivière, A. Castel, G. Lacrampe, J. Satgé, *Recl. Trav. Chem. Pays-Bas*, 102 (1983) 65.
- 44 M. Rivière-Baudet, A. Khallaayoun, J. Satgé, *Recl. Trav. Chem. Pays-Bas*, 107 (1988) 152.
- 45 M. Rivière-Baudet, P. Rivière, A. Khallaayoun, J. Satgé, K. Rauzy, *J. Organomet. Chem.*, 358 (1988) 77.
- 46 M. Rivière-Baudet, J. Satgé, K. Rauzy, *Conf. PSIBLOCS Paris-Palaiseau*, Aug. 1988., Abstract p. 23.
- 47 M. Rivière-Baudet, J. Satgé, A. Morère, *J. Organomet. Chem.* 386 (1990) C7
- 48 T. Tsumuraya, W. Ando, *Chem. Lett.*, (1989) 403.
- 49 J. Pfeiffer, W. Maringgele, M. Noltemeyer, A. Meller, *Chem. Ber.*, 122 (1989) 245.
- 50 M.F. Lappert, A.R. Sanger, P.P. Power, R.C. Srivastava, in *Metal and Metalloid Amides*, Wiley, Chichester, 1980.
- 51 J. Escudié, C. Couret, J. Satgé, J.D. Andriamizaka, *Organometallics*, 1 (1982) 1261.
- 52 C. Couret, J. Satgé, J.D. Andriamizaka, J. Escudié, *J. Organomet. Chem.*, 157 (1978) C35
- 53 J. Satgé, J. Escudié, C. Couret, H. Ranaivonjatovo, M. Andrianarison, *Phosphorus Sulfur*, 27 (1986) 65.
- 54 C. Couret, J. Escudié, J. Satgé, J.D. Andriamizaka, B. Saint-Roch, *J. Organomet. Chem.*, 182 (1979) 9.
- 55 C. Couret, J.D. Andriamizaka, J. Escudié, J. Satgé, *J. Organomet. Chem.*, 208 (1981) C3.
- 56 J. Escudié, C. Couret, J. Satgé, M. Andrianarison, J.D. Andriamizaka, *J. Am. Chem. Soc.*, 107 (1985) 3378.
- 57 H. Ranaivonjatovo, J. Escudié, C. Couret, J. Satgé, M. Dräger, *New J. Chem.*, 13 (1989) 389.
- 58 M. Dräger, J. Escudié, C. Couret, H. Ranaivonjatovo, J. Satgé, *Organometallics*, 7 (1988) 1010.
- 59 M. Andrianarison, C. Couret, J. P. Declercq, A. Dubourg, J. Escudié, H. Ranaivonjatovo, J. Satgé, *Organometallics*, 7 (1988) 1545.
- 60 G. Fritz, K.D. Hoppe, W. Honle, D. Weber, C. Mujica, V. Manriquez, H.G. von Schnering, *J. Organomet. Chem.*, 249 (1983) 63.
- 61 K.F. Tebbe, B. Freckmann, *Acta Crystallogr.*, C40 (1984) 254.

- 62 M. Andrianarison, C. Couret, J.P. Declercq, A. Dubourg, J. Escudié, J. Satgé, *J. Chem. Soc., Chem. Commun.*, (1987) 921.
- 63 J. Escudié, C. Couret, M. Andrianarison, J. Satgé, *J. Am. Chem. Soc.*, 109 (1987) 386.
- 64 J. Escudié, C. Couret, M. Andrianarison, A. Raharinirina, J. Satgé, *Phosphorus Sulfur*, 30 (1987) 377.
- 65 C. Couret, J. Escudié, J. Satgé, A. Raharinirina, J.D. Andriamizaka, *J. Am. Chem. Soc.*, 107 (1985) 8280.
- 66 C.N. Smit, F. Bickelhaupt, *Organometallics*, 6 (1987) 1156.
- 67 J. Escudié, C. Couret, A. Raharinirina, J. Satgé, *New J. Chem.*, 11 (1987) 628.
- 68 L. Lange, B. Meyer, W.W. DuMont, *J. Organomet. Chem.*, 329 (1987) C17.
- 69 J. Barrau, G. Rima, J. Satgé, *J. Organomet. Chem.*, 252 (1983) C73.
- 70 J. Barrau, G. Rima, M. El Amine, J. Satgé, *J. Organomet. Chem.*, 345 (1988) 39.
- 71 J. Barrau, N. Ben Hamida, J. Satgé, *J. Organomet. Chem.*, 282 (1985) 315.
- 72 J. Barrau, N. Ben Hamida, A. Agrebi, J. Satgé, *Organometallics*, 6 (1987) 659.
- 73 J. Barrau, N. Ben Hamida, A. Agrebi, J. Satgé, *Organometallics*, 8 (1989) 1585.
- 74 J. Barrau, M. El Amine, G. Rima, J. Satgé, *Can. J. Chem.*, 64 (1986) 615.
- 75 J. Barrau, G. Rima, M. El Amine, J. Satgé, *J. Chem. Res. (S)*, (1985) 30.
- 76 J. Barrau, M. El Amine, G. Rima, J. Satgé, *J. Organomet. Chem.*, 277 (1984) 323.
- 77 W. Ando, J. Tsumuraya, A. Sekiguchi, *Tetrahedron Lett.*, 26 (1985) 4523.
- 78 J. Barrau, G. Rima, M. El Amine, J. Satgé, *Synth. React. Inorg. Met.-Org. Chem.*, 18 (1988) 317.
- 79 A. Marchand, P. Gerval, F. Duboudin, M. Joanny, P. Mazerolles, *J. Organomet. Chem.*, 267 (1984) 93.
- 80 G. Manuel, G. Bertrand, W.P. Weber, S.A. Kazoura, *Organometallics*, 3 (1984) 1340.
- 81 K.T. Kang, G. Manuel, W.P. Weber, *Chem. Lett.*, (1986) 1685.
- 82 G. Manuel, A. Faucher, P. Mazerolles, *J. Organomet. Chem.*, 327 (1987) C25.
- 83 J. Barrau, G. Rima, H. Lavayssière, G. Dousse, J. Satgé, *J. Organomet. Chem.*, 246 (1983) 227.
- 84 J. Barrau, V. Baladji, J. Michl, *Organometallics*, 8 (1989) 2034.
- 85 M. Veith, S. Becker, V. Huch, *Angew. Chem., Int. Ed. Engl.*, 28 (1989) 1237.
- 86 J. Barrau, M. Bouchaut, H. Lavayssière, G. Dousse, J. Satgé, *J. Organomet. Chem.*, 243 (1983) 281.
- 87 H. Lavayssière, G. Dousse, J. Satgé, J. Barrau, M. Traore, *Angew. Chem., Int. Ed. Engl.*, 21 (1982) 447.
- 88 H. Lavayssière, J. Satgé, J. Barrau, M. Traore, *J. Organomet. Chem.*, 240 (1982) 335.
- 89 G. Trinquier, M. Pelissier, B. Saint-Roch, H. Lavayssière, *J. Organomet. Chem.*, 214 (1981) 169.
- 90 C. Guimon, G. Pfister-Guillouzo, H. Lavayssière, G. Dousse, J. Barrau, J. Satgé, *J. Organomet. Chem.*, 249 (1983) C17.
- 91 J.L. Garcia, D. Gonbeau, G. Pfister-Guillouzo, M. Roch, J. Weber, *Can. J. Chem.*, 63 (1985) 1518.
- 92 C. Guimon, G. Pfister-Guillouzo, G. Rima, M. El Amine, J. Barrau, *Spectrosc. Lett.* 18 (1985) 7.
- 93 G. Pfister-Guillouzo, C. Guimon, *Phosphorus Sulfur*, 23 (1985) 197.
- 94 M. Veith, M. Grosser, *Z. Naturforsch.*, 37b (1982) 1375.