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Stable germanium analogs of carbenes, imines, ketones, thiones, selones and tellones

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Abstract

The chemistry of low coordinate germanium compounds has made important advances in recent years and a rather large number of these species have been isolated in a monomeric state owing to both electronic and/or steric effects. This review reports with their synthetic routes the stable germylenes $>$Ge and the stable germanimines, germanone, germanethiones, -selones and -tellones $>$Ge=Y (Y=N–, O, S, Se, Te) prepared up to now, focusing particularly on compounds whose structures have been determined. © 1998 Elsevier Science S.A. All rights reserved.

Keywords: Germanium compounds; Stable germylenes

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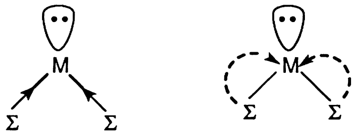
1. Introduction

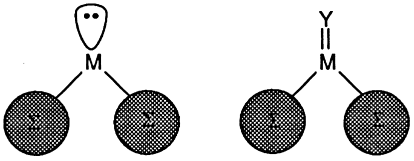
The existence of low coordination compounds of group 14 elements has been contested for a long time in the literature. It is only recently, that stable divalent species [$>M_{14}$] and species involving metal π-bonds were found to exist. The preparation of divalent tin compounds, however, was reported almost 130 years ago [1] and the first mention of dimethylsilicon oxide appeared in 1871 [2]. Around 1910 several authors described the synthesis of $Ph_2Si{=}CH_2$ [3] and $Me_2Si{=}O$ [4,5]. The structures of these compounds were inferred from indirect methods of analysis and in fact all were polymeric in nature. The notion of a stable divalent species bearing organic substituents reappeared in 1956, with the synthesis by Fischer of dicyclopentadienyltin Cp_2Sn [6], but the concept of group 14 elements species bonded by π-bonds has long been contested. From theoretical studies, it was confirmed that the derivatives of the type $>M{=}Y$ could not exist as stable entities as noted in a book published in 1965 titled Non Existent Compounds [7]. In 1966 Gusel'Nikov and coworkers demonstrated conclusively that dimethylsilene arose from the pyrolysis of silacyclobutanes [8–10]. Since then, the chemical investigation of group 14 metal species with low coordination numbers has proven to be a rich area for research. It has been demonstrated that many such species are present either in transition states or as intermediates in numerous reaction processes; in certain cases these may be sufficiently stable to be isolated as pure entities. In fact, group 14 elements species with a low degree of coordination are not intrinsically unstable, but it is difficult to isolate such species because of their elevated reactivity. Use of various ligands to improve this stability has been investigated and in the last two decades the chemistry of thermally stable divalent or doubly bonded compounds of the group 14 elements has developed into an active area of research.

The four principal methods of their stabilization are:

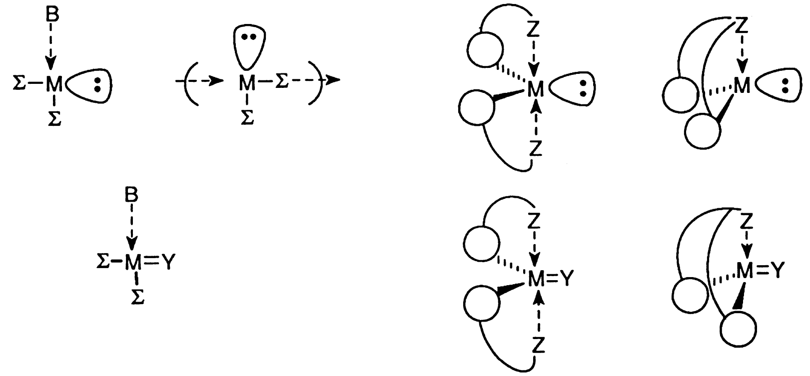
(1) The use of ligands that are n- or π-donors to the group 14 elements.



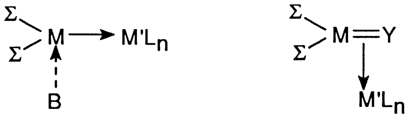
(2) The use of bulky groups bonded to M_{14}.



(3) The coordination of a donor (Lewis base) B on the metal center.



(4) The complexation with a transition metal.



It is noteworthy that compounds of the type Σ_2M or $\Sigma_2M{=}Y$ obtained in a monomeric state using methods (3) and (4) are not really analogs of the carbenes or of imines, ketones, thiones, selones and tellones given that these metal atoms possess at least eight or ten valence electrons, respectively.

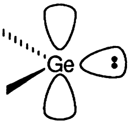
The group 14 elements derivatives which have a low degree of coordination have been the subject of several reviews [11–42]. Refs. [11–29] focus particularly on divalent species, while Refs. [18,19,30–42] concentrate on tricoordinate M_{14} species. In the present review, we shall limit ourselves to the subject of **stable** low coordinate germanium compounds including **germylenes**, **germanimines**, **germanone**, **germanethiones**, **-selones and -tellones** examining in particular stable model compounds whose structures have been determined using X-ray crystallographic analysis. The reactivity of these species is not reviewed in this paper, nevertheless, due to their high potential in organometallic chemistry, their main chemical properties will be summarized in two brief subsections.

(The section dealing with the divalent species is organized in two parts: thermodynamic and kinetic stabilization, bearing in mind that both steric and electronic factors can be invoked as stabilizing factors for some of the reported compounds.)

2. Divalent species $>$Ge

2.1. General

The divalent germanium species $>$Ge are analogs of carbenes; *ab initio* calculations [43] and spectroscopic studies [44–46] have shown that the singlet state is energetically favored for the germylenes; the triplet state lies at a higher energy. In general, they are short-lived intermediates with very high reactivity.



Dihalogermylenes X_2Ge were the first known and studied divalent species [18]; subsequently numerous functional germylenes (mixed RGeX, RGeY, XGeY, symmetrical acyclic and cyclic R_2Ge, Y_2Ge) were been reported as derivatives or intermediates [11]. Now the chemistry of germylenes is notably developed and a series of reviews or general articles cover the synthetic methods leading to these species and their use as synthetic starting materials and intermediates in organogermanium chemistry [11,16–29].

As a general rule, when these species contain unfunctionalized organic ligands, they undergo rapid oligomerization or polymerization. Sterically demanding substituents have been used to prevent the aggregation of these species but the ligand backbone may also play an important role in improving the stability. Thus various germylenes kinetically and/or thermodynamically stabilized have been isolated.

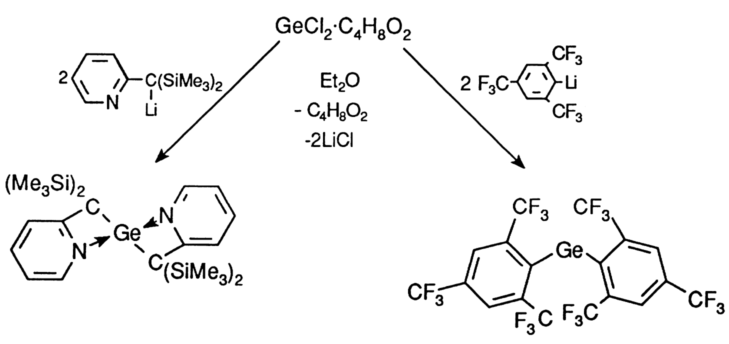
2.2. Thermodynamic stabilization

The presence of ligands which are n- or π-donors on the germanium can, by transfer of electron density from the ligand into empty p-orbitals on germanium, reduce the electronic deficit on the central atom. Many different stable divalent germanium species have been prepared taking advantage of this approach.

2.2.1. Dialkyl- and diarylgermylenes R_2Ge

(i) The bis[(2-pyridyl)bis(trimethylsilyl)methyl-*C*,*N*]germanium(II) compound is the first example of a base stabilized dialkylgermylene. This germylene was prepared by reaction of lithiated 2-[bis(trimethylsilyl)methyl]pyridine and $GeCl_2 \cdot C_4H_8O_2$ in ether at -78 °C (Scheme 1). The structure of the product was determined by an X-ray diffraction study [47]. The Ge–N distance (2.273 Å) possesses dative character; while the pyridine ring of the 2-methylpyridyl ligand shows typical values for an aromatic system.

(ii) The fluoroarylgermylene bis[2,4,6-tris(trifluoromethyl)phenyl]germanium(II) compound has recently been synthesized by the reaction of two equivalents of [2,4,6-tris(fluoromethyl)phenyl]lithium with $GeCl_2 \cdot$dioxane [48] (Scheme 1).



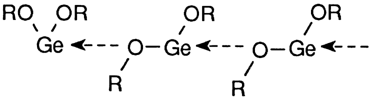
Scheme 1.

This monomeric germylene has good thermal stability, despite having the least sterically encumbering set of stabilizing ligands of any alkyl germylene isolated to date. The X-ray study indicates that the aryl rings are twisted from coplanarity and four close intramolecular Ge–F contacts are observed. The stabilizing influence of the 2,4,6-tris(trifluoromethyl)phenyl ligand is only partly due to steric protection. Despite the electron-withdrawing character of the trifluoromethyl group, the electron donation from the fluorine atom to the germanium is clearly established and is probably the most important stabilizing factor.

2.2.2. *Germylenes Y_2Ge ($Y=NR_2$, PR_2, OR, SR)*

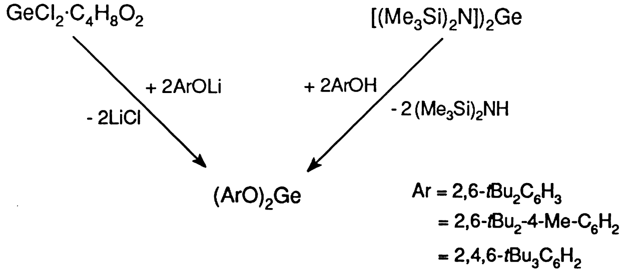
The principal route to difunctional germylenes involves nucleophilic substitution reactions of other difunctional germylenes such as those involving deshydrohalogenation from dichlorogermylenes, transesterification of alkoxygermylenes, and via the ligand exchange reactions of alkoxy-, amino- and bis(cyclopentadienyl)germylenes [18,19].

2.2.2.1. Alkoxy- and aryloxygermylenes $Ge(OR)_2$. (i) Numerous alkoxy- and aryloxygermylenes have been reported in the literature [18,19]. These are, in general, associated oligomers in a liquid state.

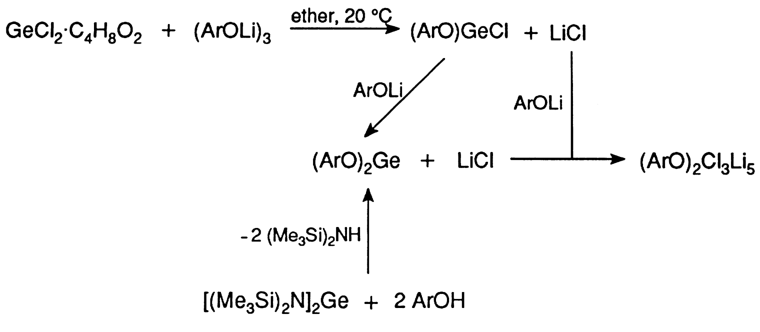


(ii) A series of different crystalline aryloxygermylenes which are monomeric at ambient temperature have been obtained by Lappert [49] as shown in Scheme 2.

(iii) The synthesis and characterization of a new stable bivalent homoleptic germanium species $(ArO)_2Ge$ [$Ar=2,4,6\text{-}[(CH_3)_2NCH_2]_3C_6H_2$] has been described recently [50,51]. This germylene has been obtained in good yield by alcoholysis with ArOH of the Ge–N bonds of the divalent precursor $[(Me_3Si)_2N]_2Ge$ (Scheme 3). The direct reaction of two equivalents of [2,4,6-tris((dimethylamino)methyl)phenoxy]lithium with the divalent species $GeCl_2 \cdot C_4H_8O_2$ results in the formation of the expected



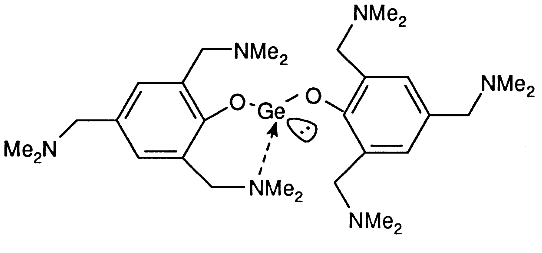
Scheme 2.



Scheme 3.

germylene along with the germylene ArOGeCl and the cluster $(ArO)_2Cl_3Li_5$ (Scheme 3).

The coordination behavior of the (dimethylamino)methyl side chains to the germanium atom has been studied by VTR spectroscopy; on the NMR time scale this germylene in solution exhibits a temperature dependent $N \cdots Ge \cdots N$ coordination mode.



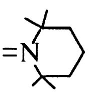
2.2.2.2. Thioalcoxygermylenes $Ge(SR)_2$. Thioalcoxygermylenes appear to be relatively unstable; thus, the germylene $Ge(SMe)_2$ could not be isolated in a monomeric state. All synthetic approaches to this compound have led to polymers [52,53]. However, Jutzi and Steiner have successfully prepared a variety of thioalcoxygermylenes [54] (Eq. (1)).

$$GeCl_2 \cdot C_4H_8O_2 + 2Me_3SiSR \underset{-C_4H_8O_2}{\rightarrow} Ge(SR)_2 + 2Me_3SiCl \qquad (1)$$
$$R = C_6H_5,\ C_6H_5CH_2,\ n-C_4H_9$$

These divalent germanium species exist as dimeric or trimeric associated forms.

2.2.2.3. Aminogermylenes $Ge(NR_2)_2$. Lappert *et al.* have obtained many compounds of the type $Ge(NR_2)_2$ [44,55,56]. These germylenes are typically distillable oils or solids, which are monomeric in solutions and exhibit thermochromic properties (Eq. (2)).

$$GeCl_2{\cdot}C_4H_8O_2 + 2\ RR'NLi \xrightarrow[-C_4H_8O_2]{} (R_2N)(R'_2N)Ge\ +\ 2\ LiCl$$
$$R=R'=Me_3Si,Me_3Ge,Et_3Ge,Et_3Si,Ph_3Ge \qquad (2)$$
$$R=tBu;R'=Me_3Si \qquad R=tBu;R'_2N=$$



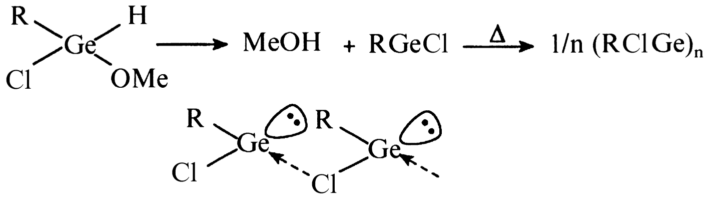
2.2.2.4. Phosphinogermylenes (diphosphanylgermylenes). Diverse phosphanylgermylenes, like their oxygen, sulfur and nitrogen homologs have been described. They are usually found to be associated oligomers [18,19] and less frequently in monomeric form. Thus, the transmetallation reaction of (fluorosilyl)silylphosphanyles $R_1R_2PLi(THF)_2$ with GeI_2 leads to diphosphanylgermylenes of the type $Ge(PR_1R_2)$ which were isolated as green crystals [57] (Eq. (3)).

$$R_1R_2PLi(THF)_2 + GeI_2 \underset{-78\ {\circ}C}{\overset{toluene}{\rightarrow}} (R_1R_2P)_2Ge$$
$$R_1 = [2,4,6\text{-}(Me_2CH)_3C_6H_2]_2(F)Si,\ R_2 = (Me_2CH)_3Si \qquad (3)$$
$$R_2 = [2,4,6\text{-}(Me_2CH)_3C_6H_2](F)(Me_3C)Si,\ R_2 = (Me_2CH)_3Si$$

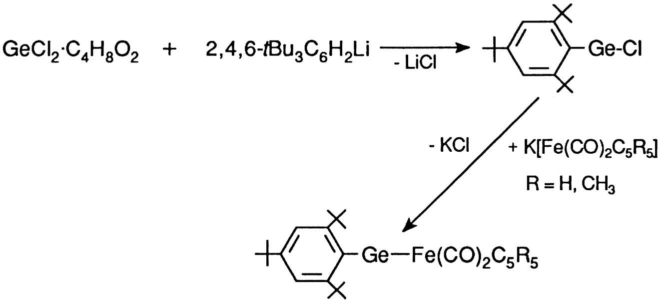
2.2.3. Mixed germylenes RGeX, RGeY and XGeY

(i) Heteroleptic germylenes, EtGeCl and PhGeCl, have been isolated in a non-polymeric form as viscous oils. This may result from an intermolecular association, through coordination interactions between the halogen lone pair and vacant 3p orbitals on germanium, which stabilizes the germylene in a partially condensed form. On heating, the germylene polymerizes to a polygermane [11,18,19] (Eq. (4)).

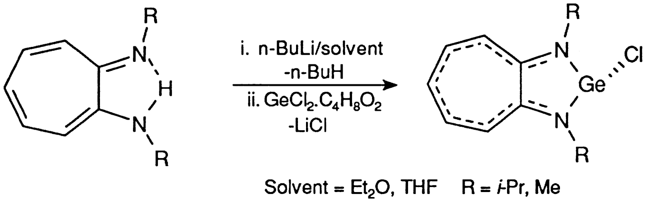
(ii) The chlorosupermesitylgermylene Mes*GeCl (Mes* = 2,4,6-tBu$_3$C$_6$H$_2$) unlike other RGeCl derivatives, was obtained as yellow crystals which were shown to be monomeric. The stability of this germylene is explained in terms of the pronounced steric hindrance of the supermesityl ligand. Furthermore, thermodynamic stabilization due to an intramolecular Cl→Ge back-bonding seems possible. This compound serves as a starting material for the related supermesitylferrogermylene [58] (Scheme 4).



(4)



Scheme 4.

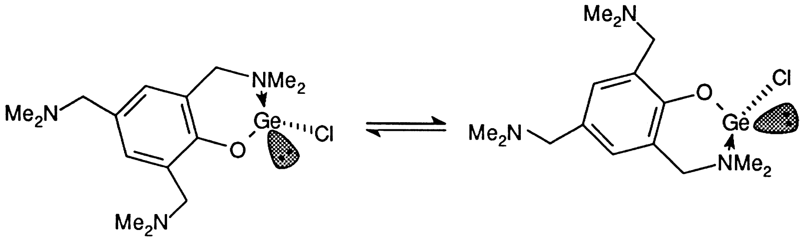


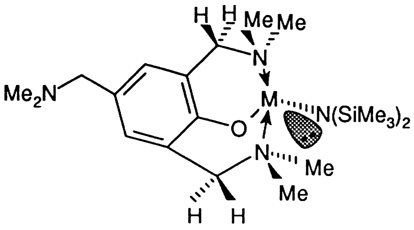
Scheme 5.

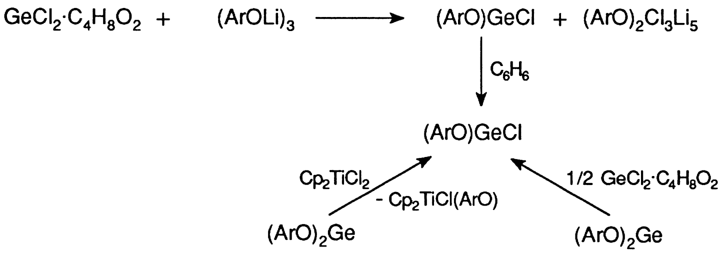
(iii) Aminotroponimate (ATI) derivatives of germanium(II) have also been investigated. The synthesis of the germanium(II) chlorides [(*i*-Pr)$_2$ATI]GeCl and [(Me)$_2$ATI]GeCl was achieved by the treatment of $GeCl_2 \cdot C_4H_8O_2$ with [(*i*-Pr)$_2$ATI]Li or [(Me)$_2$ATI]Li in a 1:1 molar ratio in diethyl ether or THF; they were isolated in stable orange crystalline forms [59] (Scheme 5). One of the interesting features of aminotroponiminato derivatives of Ge(II) is the planar bicyclic 10-π-electrons ring system.

(iv) Two other heteroleptic structures (ArO)XGe [Ar=2,4,6-[$(CH_3)_2NCH_2]_3C_6H_2$; X=Cl, N(SiMe$_3$)$_2$] in which the metal has also a prochiral structure have been reported [50,51,60] (Schemes 6 and 7).

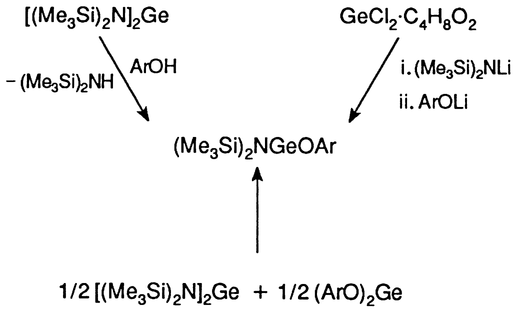
According to ^{1}H NMR data, various intramolecular complexation modes of the germanium atom have been observed, depending on the nature of the X ligand. In the (ArO)ClGe case, a dynamic N$\cdots$Ge$\cdots$N coordination mode is observed, while in the (ArO)[(Me$_3$Si)$_2$N]Ge case, the two *o*-N atoms of the aryloxy ligand are involved in a static coordination to the germanium atom.







Scheme 6.



Scheme 7.

(v) A monoarylchlorogermylene 2,6-$Mes_2C_6H_3GeCl$ has recently been reported by Power [61]. It is the first fully characterized chlorogermylene in which the organic ligand is monodentate, purely σ-bonded and non-chelating. But it is noteworthy that in the solid state this germylene has a dimeric structure in which the monomers are linked by a relatively weak 2.44 Å Ge–Ge interaction (see Section 2.3.2 (iii)).

2.2.4. Sandwich Cp^*_2Ge, semi-sandwich $RGeCp^*$ and $XGeCp^*$ germylenes

(i) The germanocene $(C_5H_5)_2Ge$, the first π-complex of germanium, was obtained by Curtis and Scibelli in 1973 [62]. Following this approach, diverse germanocenes with substituted cyclopentadienyl ligands have been synthesized [26–29,63,64] following the route shown in Eq. (5).

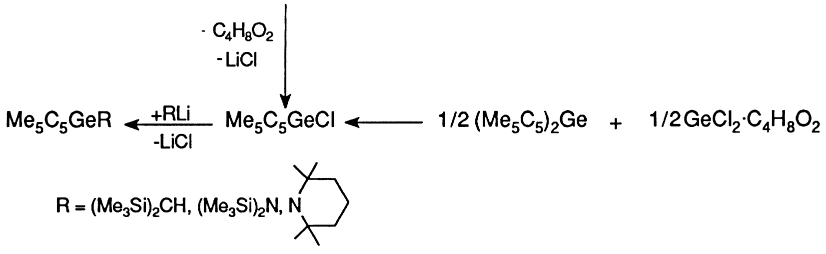
$$\begin{gathered} GeX_2 + 2MC_5R_5 \underset{-2MCl}{\rightarrow} (R_5C_5)_2Ge \\ R_5C_5 = H_5C_5,\ MeH_4C_5,\ [(Me_3Si)_nH_{5-n}C_5]Ge \\ (R_5C_5)_2 = Me_4C_5\text{–}SiMe_2(CH)_2SiMe_2\text{–}C_5Me_4 \end{gathered} \tag{5}$$

(ii) Mixed germanocenes may be obtained by the metathesis reaction between chloropentamethylcyclopentadienylgermylene and cyclopentadienylpotassium derivatives (Eq. (6)).

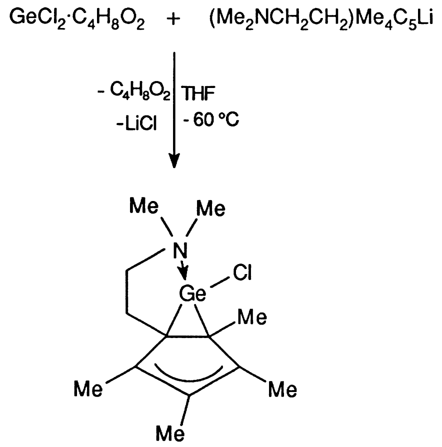
$$\begin{gathered} Me_5C_5GeCl + KC_5H_2R_3 \underset{-KCl}{\rightarrow} (Me_5C_5)GeC_5H_2R_3 \\ C_5H_2R_3 = (Me_3Si)_nH_{5-n}C_5 \end{gathered} \tag{6}$$

(iii) Monomeric semi-sandwich germylenes Me_5C_5GeR are equally accessible starting from mixed germylenes Me_5C_5GeCl [26–29,63,64] (Scheme 8).

(iv) More recently, a germylene with a dimethylamino substituted cyclopentadienyl ligand $(Me_2N\text{–}CH_2CH_2)Me_4C_5GeCl$ was described [65]. The stability against air of this germylene is strongly increased compared with the stability of Me_5C_5GeCl. The ^1H and ^{13}C NMR spectra are in accord with a highly fluxional structure in solution. In the solid state the Ge–N bond length is 2.286 Å. The structure of the compounds involved the coordination to the Ge(II) atom of the nitrogen atom from the (dimethylamino)ethyl group (Scheme 9).



Scheme 8.



Scheme 9.

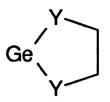
(v) The cyclopentadienyl ligand is particularly useful because the germylenes bearing it react with both nucleophilic and electrophilic reagents to give new divalent germanium species [66] (Eqs. (7) and (8)).

$$(Me_3Si)_2CHGeC_5Me_5 + LiC(SiMe_3)_3 \rightarrow (Me_3Si)_2CHGeC(SiMe_3)_3 + Me_5C_5Li \tag{7}$$

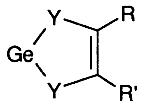
$$(Me_3Si)_3CGeC_5Me_5 + HCl \rightarrow (Me_3Si)_2CGe(H)(Cl)C_5Me_5 \xrightarrow[-Me_5C_5H]{} (Me_3Si)_3CGeCl \tag{8}$$

2.2.5. *Cyclic and macrocyclic germylenes*

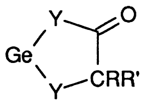
(i) Several cyclopentane-derived heterocyclic germylenes containing oxygen, sulfur or phosphorus have been described [67–70]. They are generally found in an associated (oligomeric) form.



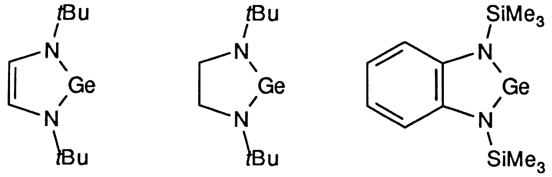
Y = O, S, PPh



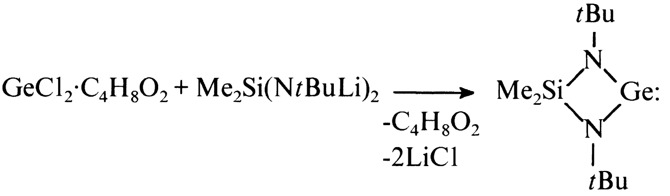
Y = O, S
R = Me, Et, Ph
R' = H, Ph, CN



(ii) Those cyclic or macrocyclic germylenes which are monomers in solution are essentially found only in the case of germylenes containing the Ge–N bond [44,71–73].



(iii) One should, in particular, cite the work of Veith [74–78] concerning two cyclic and polycyclic germylenes which contain many metal centers (Eqs. (9) and (10)).



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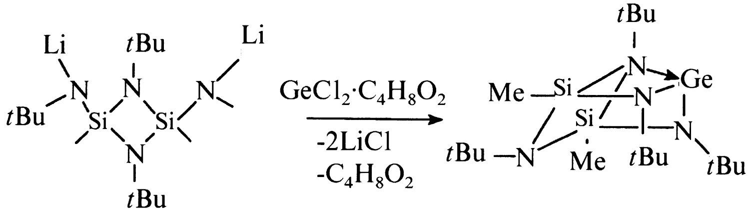


(10)

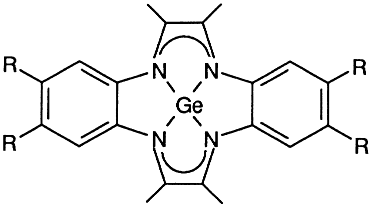
The stabilization of the latter germylene (Eq. (10)) by the intramolecular coordination of a base to the germanium atom is noteworthy.

(iv) Parkin [79] and Cowley [80] introduced the use of tetraazamacrocyclic ligands such as the dibenzooctamethyltetraaza[14]annulene (Me_8taa) and dibenzooctamethyltetraaza[14]annulene (Me_4taa) for stabilizing divalent germanium species (Eq. (11)).

$$GeCl_2 \cdot C_4H_8O_2 + Me_n taaLi_2 \underset{\text{-2LiCl}}{\overset{Et_2O,\ -78\ \circ C}{\rightarrow}} Ge(Me_n taa) \qquad (11)$$

$$n = 4,\ 8$$

These red crystalline compounds are characterized by the atom of germanium that lies, symmetrically, between the four nitrogen atoms in the macrocycle.



Me_4taa R = H
Me_8taa R = Me

2.3. Kinetic stabilization

Electronic factors may be invoked to explain the stability of the germylene described in the preceding section. However, the intervention of steric factors in these molecules resulting in kinetic stabilization should not be overlooked. One can note, for example, the protection afforded to the germanium atom by bulky groups, in particular, the germylenes reported by Lappert which are stabilized by bulky amino groups.

In fact, there are several examples of germylenes whose stability rests exclusively on steric factors.

2.3.1. Dialkylgermylenes

(i) The germylene of Lappert Ge[CH$(SiMe_3)_2]_2$, obtained by the ligand metathesis starting from Ge[N$(SiMe_3)_2]_2$ (Eq. (12)) or by Grignard reaction starting from $GeCl_2 \cdot C_4H_8O_2$, is monomeric both in solution and the gas phase [81,82].

$$2(Me_3Si)_2CHLi + Ge[N(SiMe_3)_2]_2 \rightarrow Ge[CH(SiMe_3)_2]_2 + 2LiN(SiMe_3)_2 \qquad (12)$$

However, an X-ray crystal study showed that the CH$(SiMe_3)_2$ ligands were insufficiently bulky to prevent the dimerization in the solid state [83].

(ii) The substitution of just one of these CH$(SiMe_3)_2$ ligands by the group C$(SiMe_3)_3$, which introduces almost the same steric bulk, is sufficient to stabilize the mixed germylene in a monomeric form in the solid state [84] (Eq. (13)).

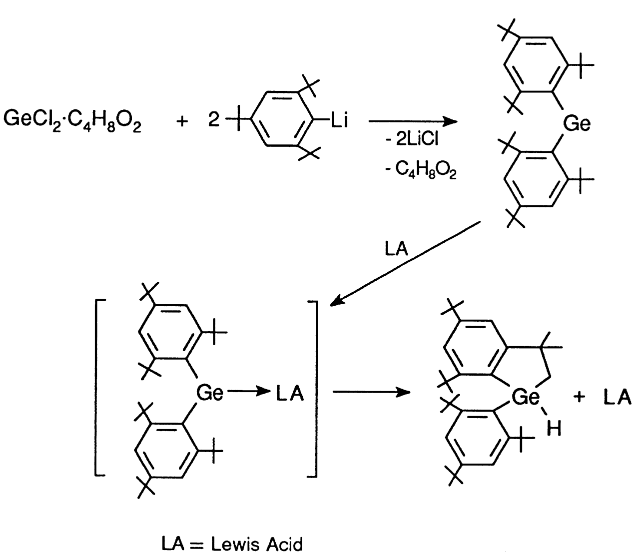
$$\begin{array}{c} Me_5C_5GeCH(SiMe_3)_2 + (Me_3Si)_3CLi.2THF \\ \text{-2THF}\Big\downarrow \\ Ge[CH(SiMe_3)_2][C(SiMe_3)_3] + Me_5C_5Li \end{array} \qquad (13)$$

2.3.2. Diarylgermylenes

The stabilization afforded by aryl groups depends only on steric hindrance. In effect, all the germylenes which bear aryl groups slightly protecting, in a steric sense, are transient species [85].

(i) The first stable, monomeric, arylgermylene Mes$^*_2$Ge (Mes* = 2,4,6-tri-*tert*-butylphenyl) was first reported in 1987 [86,87] as a compound which decomposes at room temperature by insertion of the germanium atom into a C–H bond of an adjacent *o-tert*-butyl group. In fact Mes$^*_2$Ge is stable under ordinary conditions and such a C–H insertion does occur in solution forming a germaindane, but only in the presence of a Lewis acid such as the starting material $GeCl_2$ [88] (Scheme 10)

(ii) Okazaki and Tokitoh have studied diverse arylgermylenes bearing bulky groups Tbt(Ar)Ge [Tbt = 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl and Ar = mesi-

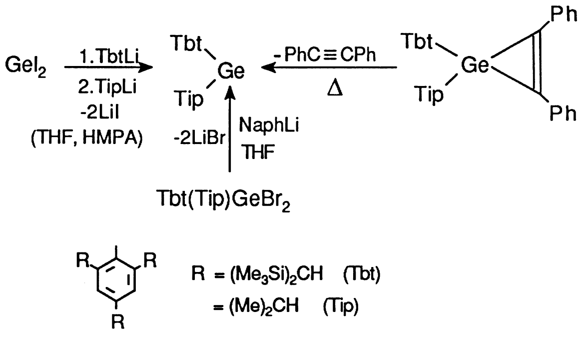


Scheme 10.

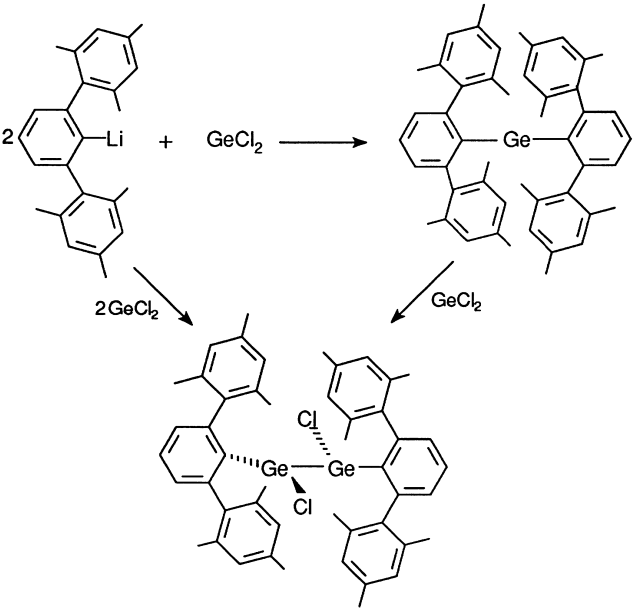
tyl or 2,4,6-triisopropylphenyl = Tip]. The introduction of the Tbt group and a mesityl (Mes) group is not sufficient to stabilize the germylene, one must replace the Mes group by a yet more overcrowded group such as Tip in order to obtain a divalent species which is stable up to 60 °C [89,90] (Scheme 11).

(iii) Recently, Power has obtained the monomeric diaryl- and monoarylgermylenes $(2,6\text{-}Mes_2C_6H_3)_2Ge$ and $Cl(2,6\text{-}Mes_2C_6H_3)Ge$ [61] (Scheme 12).

$(2,6\text{-}Mes_2C_6H_3)_2Ge$ is a thermally stable, purple, crystalline solid with V-shaped geometry. The remarkably wide (ca. 114.5°) interligand bond angle is evidence of steric crowding that is significantly greater than that observed in other σ-bonded diorganogermanium derivatives. But the monoaryl germanium chloride has a dimeric structure in which the monomers are linked by a relative weak, 2.44 Å Ge–Ge interaction.



Scheme 11.

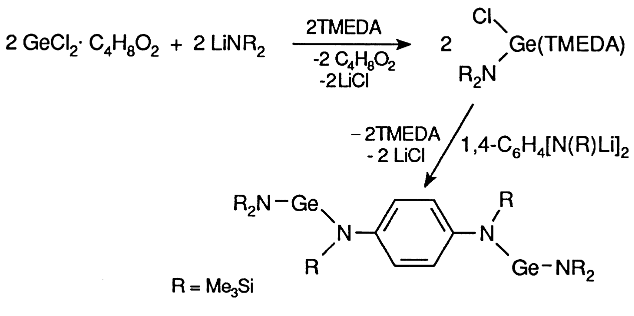


Scheme 12.

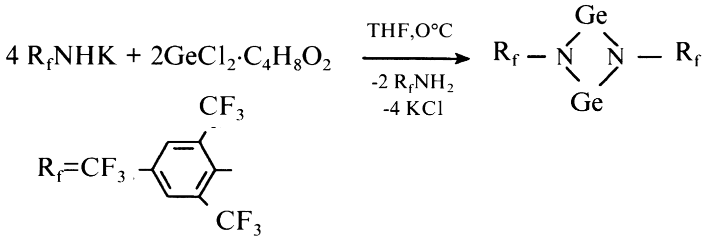
2.4. Digermylenes

(i) The first stable digermylene has been recently described by two different groups [91,92]; it is a di(diaminogermylene) with an acyclic structure obtained by a one-pot, two-step ligand substitution reactions from $GeCl_2 \cdot C_4H_8O_2$ (Scheme 13).

(ii) Using the [2,4,6-tris(trifluoromethyl)phenyl]amino group $[2,4,6\text{-}(CF_3)_3C_6H_2]N$ Roesky *et al.* have more recently taken advantage of the stabilizing properties of the [2,4,6-tris(trifluoromethyl)phenyl]amino group for the synthesis of a diazadigermetidine digermylene [120] (Eq. (14)).



Scheme 13.



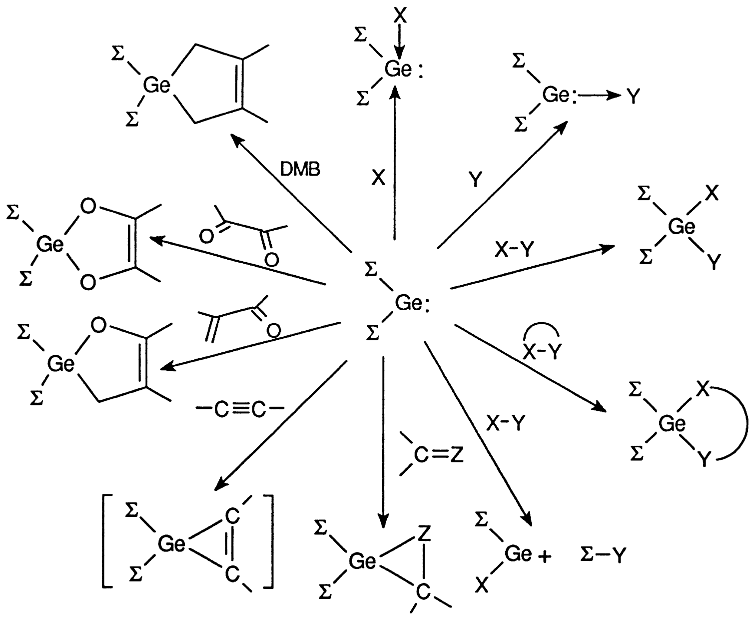
(14)

This compound crystallizes in a fluorescent-yellow orthorhombic and a yellow monoclinic crystal modification. The molecule structure is characterized by interactions of fluorine atoms of the *ortho* CF_3 groups with the metal.

2.5. Reactivity of germylenes

Due to their "carbene-like" character these divalent entities are particularly reactive and different kind of reactions have been observed [11–29]. These include as indicated in Scheme 14 the following:

(1) oligo- and polymerization reactions strongly influenced by bulky groups,
(2) insertion reactions in σ-bonds,
(3) addition reactions to unsaturated systems,
(4) complexation reactions with donors,
(5) complexation reactions with acceptors.



Scheme 14.

Many of these reactions are greatly hindered by both steric and/or electronic influences.

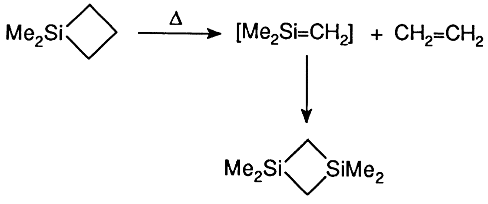
3. Species with double bond $>Ge=Y$ ($Y=N-$, O, S, Se, Te)

3.1. General

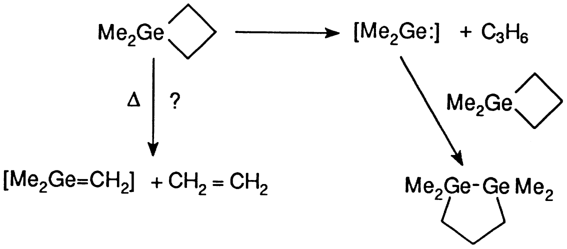
The chemistry of species with the M_{14} atom doubly bonded began to be studied almost ten years after the study of divalent species chemistry following the characterization of the dimethylsilane by pyrolysis of the silacyclobutane by Gusel'Nikov *et al.* in 1966 [8–10] (Scheme 15).

Since then, we have been witnessing a real explosion of new studies. Numerous reviews on the topic have been published, the most recent and the most comprehensive being that by Raabe and Michl [32]. The chemistry of analogous species involving germanium is, on the contrary, quite recent. The thermolysis of the dimethylgermacyclobutane has not allowed one to obtain the doubly bonded metal species [$Me_2Ge=CH_2$] [93] as in the silicon case. Instead, the decomposition of the germylated cycle occurs with the formation of mainly dimethylgermylene (Scheme 16).

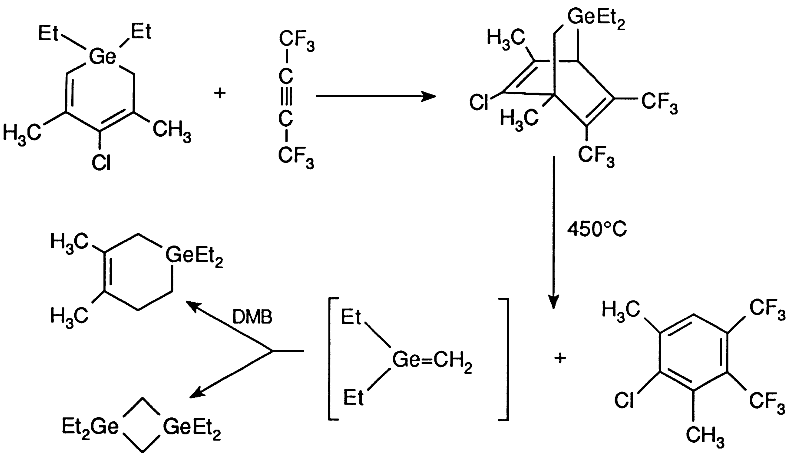
Although we notice the formation of ethylene in this thermolysis no trace of dimer (or polymer) of the dimethylgermene can be detected. In 1973, Barton *et al.* characterized the germene [$Et_2Ge=CH_2$] for the first time during the gas phase pyrolysis of the Diels–Alder adduct of germacyclohexadiene with perfluorobutyne [94] (Scheme 17).



Scheme 15.

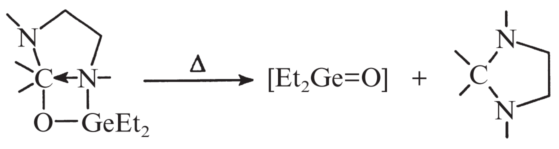


Scheme 16.



Scheme 17.

In 1977, the diethylgermanone [$Et_2Ge{=}O$] was characterized in our laboratory by the decomposition of a seven-membered heterocycle (Eq. (15)).

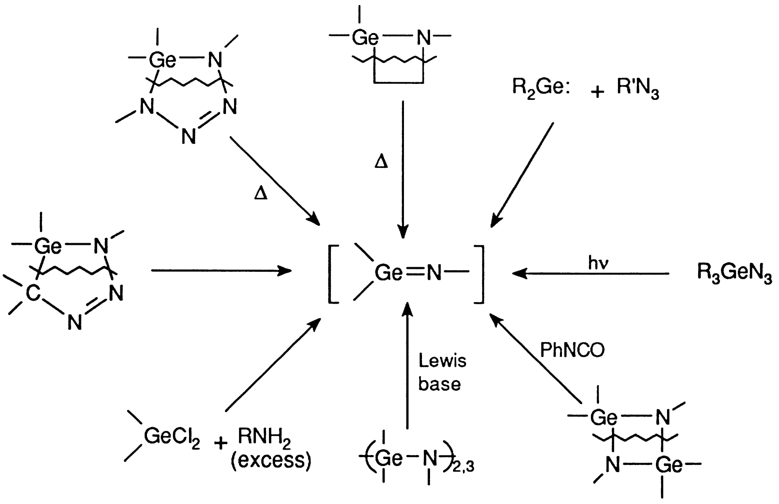


(15)

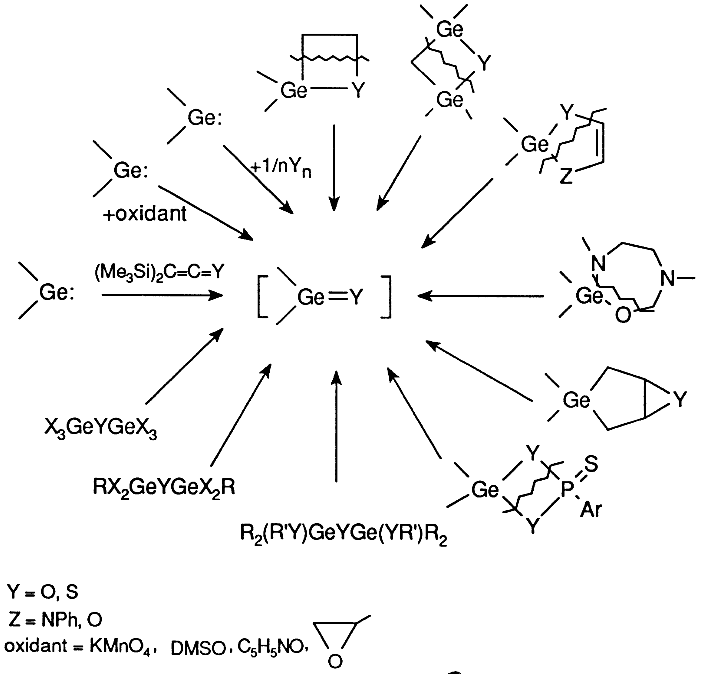
The studies of the chemistry of the germanium species [$>Ge{=}Y$] (Y=–C–, O, S, N–, P–,...) have since advanced rapidly. It may be recalled that the double bonded species of germanium are generally short-lived intermediates, highly reactive and labile; generally they must be generated *in situ*, to be chemically characterized. Several synthetic routes have been described (they are summarized by Schemes 18 and 19) and numerous aspects of their reactivity have been discussed in a number of reviews [30,31,36,39–42,95–100]. Only new salient studies from the literature on stable **germanimines**, **germanone**, **germanethiones**, **-selones and -tellones** are discussed in the present review.

3.2. Stable germanimines

Only around thirty stable germanimines have been described so far. These compounds with a germanium–nitrogen double bond can be obtained by various synthetic routes starting from germylenes, germylazides or the germane GeH_4.



Scheme 18.



Scheme 19.

3.2.1. *Reaction of germylenes with organic diazo compounds or azides*

(i) In 1987, Glidewel reported the first stable example of germanimine [101]; it was synthesized by the reaction of the germylene $[(Me_3Si)_2N]_2Ge$ with the diazomalonic ester $N_2C[C(O)OMe]_2$ according to Scheme 20.

(ii) More recently, several stable germanimines have been synthesized from germylene by reaction with azide bearing bulky groups followed by loss of nitrogen [73,103] (Eq. (16)).

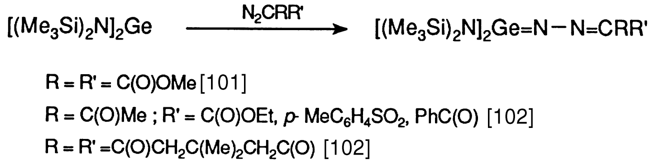
$$[(Me_3Si)_2N]_2Ge + N_3SiR_3 \xrightarrow[-N_2]{\text{THF, } 25^\circ\text{ C}} [(Me_3Si)_2N]_2Ge{=}NSiR_3 \qquad (16)$$

$$R = Et,\ OtBu$$

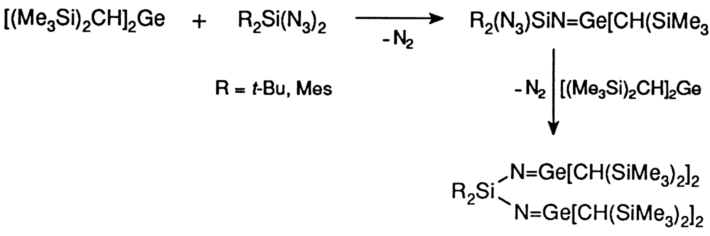
(iii) A di(germanimine) could also be obtained according to the same reactional process starting from the germanimine substituted on the nitrogen atom by the $R_2(N_3)Si$ group [104] (Scheme 21).

(iv) Following the same process, germanimines stabilized by inter- or intramolecular coordination with Lewis bases have also been isolated [105,106] (Scheme 22).

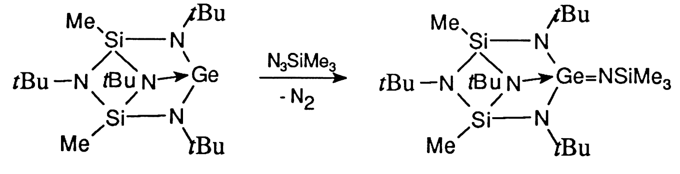
(v) The germanimine $(ArO)_2Ge{=}N{-}SiMe_3$ [50,51,107] has also been obtained in good yield by reaction of the divalent species $(ArO)_2Ge$ with trimethylsilylazide



Scheme 20.



Scheme 21.



Scheme 22.

Me_3SiN_3 (Scheme 23). In this reaction we could not detect any traces of tetraazene resulting from the 1–3 addition of the germanimine to the trimethylsilylazide as has already been observed.

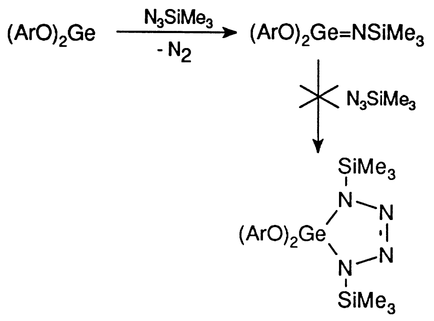
3.2.2. *Deshydrohalogenation of halogermylamines*

(i) Mesityl substituted germanimines could be obtained by deshydrohalogenation reaction from corresponding halogermylamines [108–111]. Their stability can be explained by conjugation and/or intramolecular coordination [108–110] (Scheme 24).

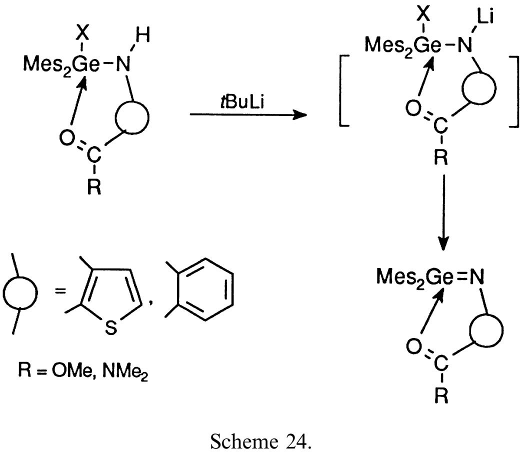
(ii) The use of the 2,4,6-trifluorophenyl (*t*FP) group on nitrogen has also been successful for stabilizing germanimine [111] (Scheme 25).

3.2.3. *Photolysis of germylazides*

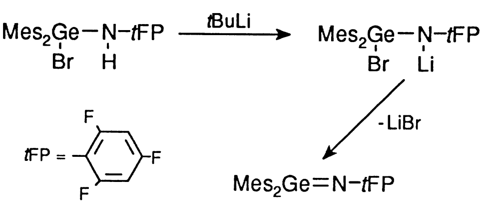
The trimesitylgermanimine $Mes_2Ge{=}N{-}Mes$ was obtained by photolysis of the corresponding trimesitylgermylazide; the formation of transient trimesitylgermylnitrene and a Curtius-type rearrangement allow one to explain the formation of the germanimine. This reaction gave rise to significant quantities of a germylated cyclic



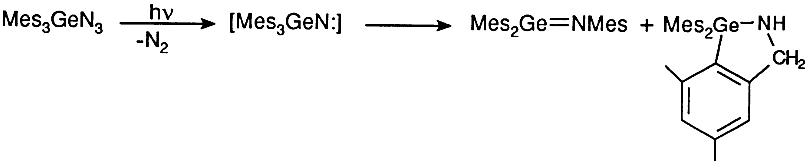
Scheme 23.



Scheme 24.



Scheme 25.

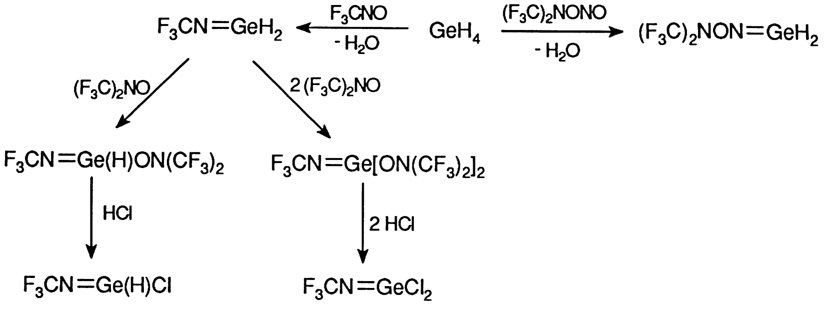


Scheme 26.

by-product which has been attributed to the intramolecular insertion of the germylnitrene function of the transient trimesitylgermylnitrene in one C–H bond of a methyl of the mesityl group [105,112] (Scheme 26).

3.2.4. *From GeH_4*

Several other germanimines having new structures have recently been synthesized by the action of germane GeH_4 on nitrosotrifluoromethane CF_3NO and on CF_3NONO [113,114]. The presence of the Ge=N bond in those derivatives has been confirmed, by infrared analysis and chemical reactivity. Surprisingly, these germanimines do not oligomerize although substituted by very small groups; this behavior might probably be due to the important effect of the trifluoromethyl groups (Scheme 27).



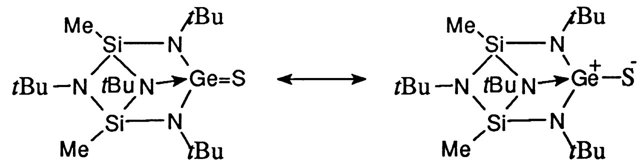
Scheme 27.

3.3. Stable germanone, germanethiones, -selones and -tellones

The chemistry of the species >Ge=Y (Y=O, S, Se, Te) essentially remains a transient species chemistry [37]. In spite of numerous attempts at stabilization, one metastable germanone, six germanethiones, five germaneselones and three germanetellones are the only species of the type >Ge=Y (Y=O, S, Se, Te) which have been isolated at room temperature, up to now.

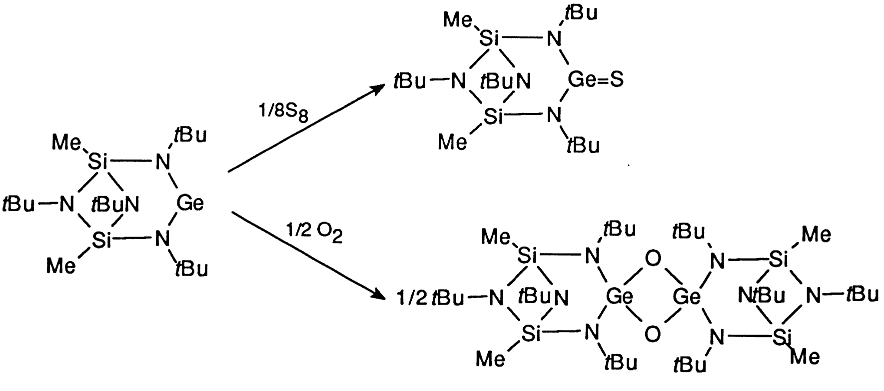
(i) The first reported synthesis of a stable compound with a Ge=Y bond appeared in 1989 [75,76]. By sulfurization of the bis(amino)germylene $(Me_2Si)_2(N\textit{t}Bu)_4Ge$, Veith *et al.* obtained a germanethione stabilized by intramolecular complexation by a Lewis base (Scheme 28).

The germanium atom in this germanethione is tetracoordinated and at this atom the geometry can be considered as being tetrahedric distorted or as being practically trigonal even with an extra bond (Ge–N). The Ge–S distance is 2.063 Å and it is shorter by about 0.2 and 0.06 Å compared to the Ge–S distances in the σ Ge–S bond of $(R_3Ge)_2S$ or of the thiogermanate anion $(Ge_4S_{10})^{4-}$, respectively. It is longer by 0.05 Å than the distance calculated for the pπ–pπ double bond of the molecule $Me_2Ge{=}S$. These authors have proposed a link between these structural properties and a molecular structure with true germanethione and zwitterionic limiting forms.



(ii) It is noteworthy that the oxidation of the same germylene leads to the dimer of the corresponding germanone (Scheme 28).

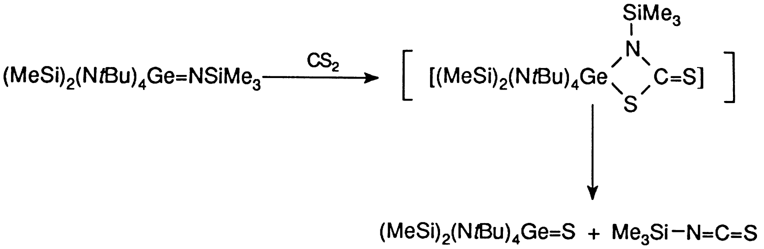
(iii) The same germanethione, $(MeSi)_2(N\textit{t}Bu)_4Ge{=}S$, has been obtained from



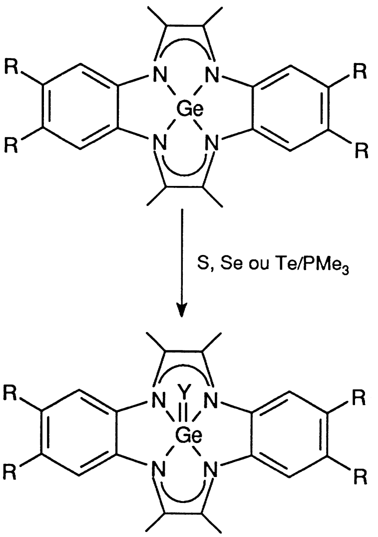
Scheme 28.

the corresponding germanimine by the action of CS_2, probably via an unstable 2-germa-4-thioxo-1,3-thiazetidine [95] (Scheme 29).

(iv) Likewise, from the germylene [Me_8taa]Ge and the elements S, Se and Te Parkin obtained the series of compounds [Me_8taa]Ge=Y (Y=S, Se, Te) [79] (Scheme 30). The X-ray structural study of these compounds displays intramolecular nucleophile coordinations which allow to consider theses species as resonance hybrids of the limiting forms $>$Ge=Y and $>$Ge$^+$–Y$^-$.



Scheme 29.



Y	d(Ge=Y)/Å	d(Ge-Y)$_{calc}$/Å	d(Ge=Y)$_{calc}$/Å
S	2.110	2.26	2.06
Se	2.247	2.39	2.19
Te	2.466	2.59	2.39

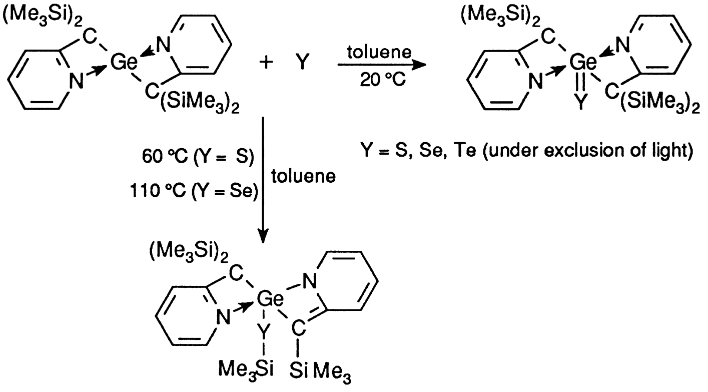
Scheme 30.

One may note that in the solid state the structures [Me_8taa]Ge=Y (Y=S, Se) are isostructural but [Me_8taa]Ge=Te adopts an inverted configuration (compared to those of Y=S, Se).

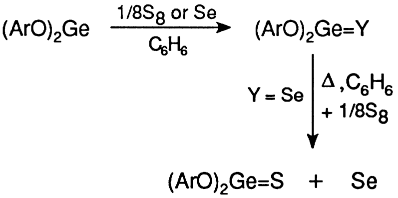
(v) Likewise, Meller starting from the bis[(2-pyridyl)bis(trimethylsilyl)methyl-*C,N*]germylene and elemental sulfur, selenium and tellure in toluene obtained the corresponding thione, selone and tellone, respectively [47,48] (Scheme 31). The tellone is thermodynamically stable; but at 60 °C for the thione, or 110 °C for the selone, one of the trimethylsilyl groups migrates to the chalcogen atom (Scheme 31).

(vi) In the same way direct confrontations of the divalent species $(ArO)_2Ge$ with Y (Y=S, Se) lead with high yields to the corresponding stable germanethione or germaneselone $(ArO)_2Ge{=}Y$ which have been physicochemically and chemically characterized [50,51,107] (Scheme 32).

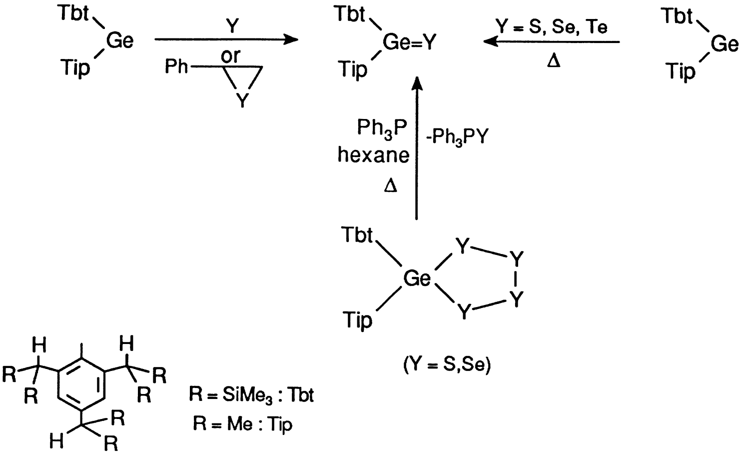
(vii) The species (Tbt)(Tip)Ge=Y (Y=S, Se, Te) lately isolated by Tokitoh and Okazaki [39,96,97,99,115–118] were the first monomeric species kinetically stabilized by steric protection offered by the very bulky groups Tbt and Tip bonded to the germanium. They could be obtained either from the corresponding germylene or from germolane- or germirene-type compounds (Scheme 33). They are stable at room temperature and can be kept under an inert atmosphere for several days. The X-ray structural analysis reveals Ge–Y bonds particularly shortened of 2.049 Å for Ge=S, 2.180 Å for Ge=Se [118] and 2.398 Å for Ge=Te [118].



Scheme 31.



Scheme 32.

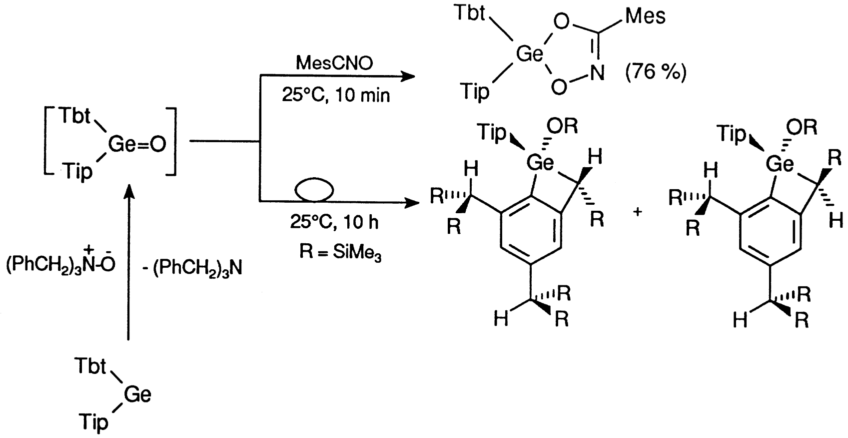


Scheme 33.

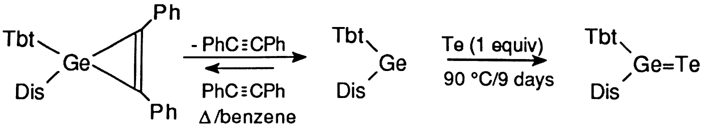
(viii) The corresponding germanone [(Tbt)(Tip)Ge=O], obtained by treatment of (Tbt)(Tip)Ge with tribenzylamine *N*-oxide [118], was stable in solution at room temperature for only a few minutes and underwent [2+3] cycloaddition with mesitonitrile oxide. In the absence of such a trapping reagent an intramolecular cyclization proceeds spontaneously leading to two diastereoisomeric benzogermacyclobutanes [119] (Scheme 34).

(ix) The synthesis and the crystalline structures of the germanium compounds with an alkyl aryl substituted three coordinated metal atom (Tbt)(Dis)Ge=Y [Y = S, Se, Te; Dis = $CH(SiMe_3)_2$] have also been described by the same group [119] (Scheme 35).

The X-ray structural analyses reveal in these cases a considerable shortening of



Scheme 34.



Scheme 35.

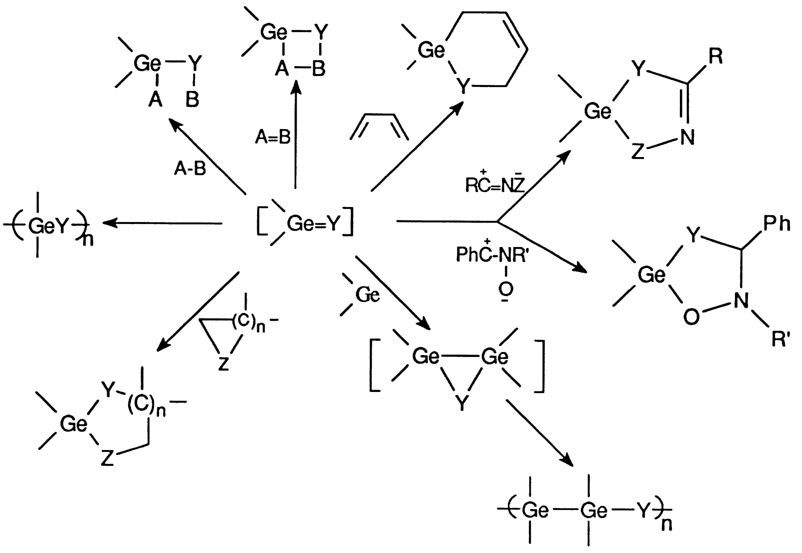
the germanium–chalcogen bonds lengths indicative of the unambiguous double bond character and complete trigonal planar geometry around the germanium atom.

The chemical behavior observed for these kinetically stabilized germanium analogs of ketones, thiones and tellones Tbt(R)Ge=Y (Y=S, Se, Te; R=Tip, Dis) is in accordance — by the steric factors — with the chemistry observed for the corresponding intermediate doubly bonded germanium species.

3.4. Reactivity of the doubly bonded species >Ge=Y

Due to the polar character of the >Ge=Y bonds the free doubly bonded species have high potential in organometallic chemistry [30,31,36,39–42,95–100]. In particular:

(1) insertion reactions,
(2) addition reactions,
(3) cycloaddition reactions,
(4) transposition reactions,
(5) polymerization reactions,



Scheme 36.

are characteristic (Scheme 36). Steric and/or electronic effects are responsible for loss of some of these characteristic aspects of the chemistry of free $>$Ge$=$Y species. [102]

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