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Silenes ⟩Si=C⟨, germenes ⟩Ge=C⟨ and stannenes ⟩Sn=C⟨
The French contribution

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Abstract

Various stable silenes $>Si{=}C<$, germenes $>Ge{=}C<$ and stannenes $>Sn{=}C<$ have been synthesized by reaction of tert-butyllithium with halovinylsilanes and -germanes (addition–elimination reactions)*. These two routes are among the most often used to synthesize stable organometallic alkenes. These derivatives, easily evidenced by their characteristic physicochemical data, are extremely reactive, much more than their alkene analogues, and appear as fruitful synthons in organic and organometallic chemistry. © 1998 Elsevier Science S.A. All rights reserved.

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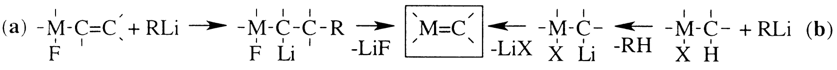
1. Introduction

The synthesis of metallaalkenes $>M{=}C<$ ($M = Si$, Ge, Sn) has interested many generations of chemists. This is due to the fact that such compounds are the heavier analogues of alkenes, which are very important organic compounds. Their synthesis and isolation appeared rapidly to be a difficult challenge because of their very great tendency to dimerize. Thus, the first stable silene $>Si{=}C<$ was only obtained in 1981 [1–3] and the first stable germenes $>Ge{=}C<$ [4–6] and stannenes $>Sn{=}C<$ [5,7] in 1987; their stabilization in a monomeric state was achieved by the use of bulky substituents both on the metal and on the carbon atoms. Since 1981, many other metallaalkenes have been obtained by various methods summarized in Scheme 1, which presents all the routes to stable silenes, germenes and stannenes.

We can see from Scheme 1 that many routes lead to silenes; however, if route **a** (from halvoinylsilanes) is probably one of the most convenient for transient silenes [8–25] [a new route involving the action of a lithium compound on $R_3Si–C(OH)R'_2$ derivatives is also very well studied [26–33]], the most available reaction paths used to produce sterically protected structures are the dehydrohalogenation reactions from halosilanes (route **b**) and the photochemical [1,3]-sigmatropic shift of a silyl group to an oxygen atom in acylsilanes (route **c**).

In contrast, only the few routes **a**, **b**, **c**, **e**, **g**, **h**, **i**, are successful for the synthesis of stable germenes and **b**, **g** for stable stannenes; the most thoroughly studied germenes have been obtained by the routes **a** and **b** and the stannenes by the route **b**.

We present in this paper the contribution of our group to the synthesis, the physicochemical investigation and the study of the reactivity of stable and isolable silenes, germenes and stannenes (or at least stable enough at room temperature to be physicochemically characterized) prepared from halosilanes, -germanes and -stannanes, by the two types of reactions **a** and **b**: addition–elimination (**a**), substitution–elimination (**b**):



$$(a)\ -\underset{F}{M}-C{=}C\langle + RLi \rightarrow -\underset{F}{M}-\underset{Li}{C}-C-R \xrightarrow[-LiF]{} \boxed{\rangle M{=}C\langle} \xleftarrow[-LiX]{} -\underset{X}{M}-\underset{Li}{C}- \xleftarrow[-RH]{} -\underset{X}{M}-\underset{H}{C}- + RLi\ (b) \qquad (1)$$

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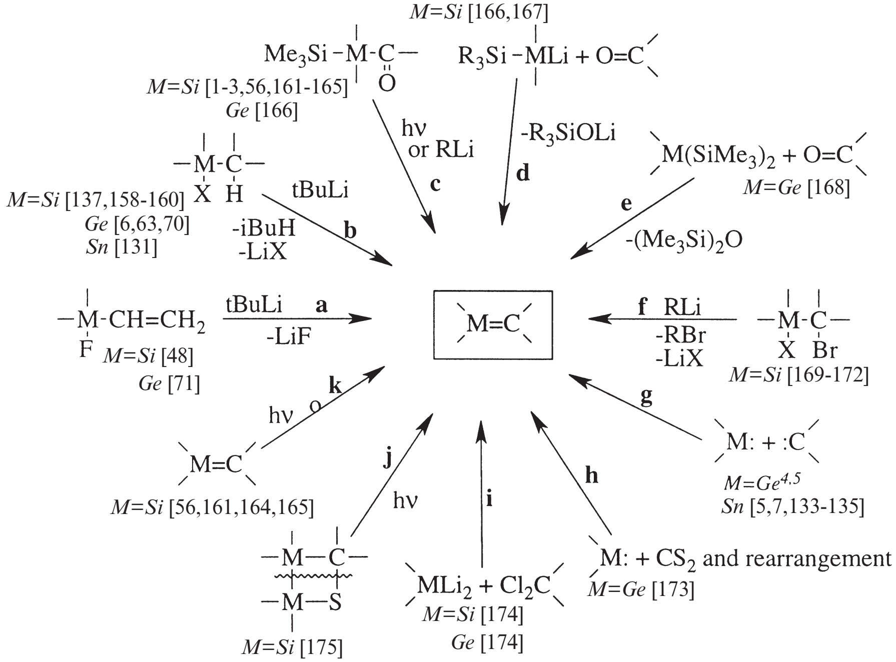
* or with halofluorenylgermanes and -stannanes (substitution-elimination reactions)



Scheme 1. All routes to stable silenes, germenes and stannenes

Many reviews have been devoted to silenes since the very detailed compilation written by Raabe and Michl in 1985 [34] concerning all transient and stable doubly bonded silicon compounds: see for example the papers by Brook and Baines [35], Cowley and Norman [36], Grev [37], Lickiss [38], Brook and Brook [39], Auner et al. [40], Chaubon et al. [41] and a book edited by Patai and Rappoport [42].

In the field of germenes, the first review, written by Satgé [43], described only transient compounds since no stable $\rangle Ge{=}C\langle$ derivatives were known at that time. Other reviews about $\rangle Ge{=}X$ compounds, including germenes, were published by Wiberg [44], some of us [41,45,46], Baines and Stibbs [47] and Grev for theoretical studies [37].

For stannenes, see the paper of Baines and Stibbs [47] and of two of us [41].

2. Addition–elimination reactions

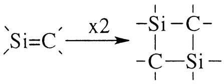
2.1. Silenes

2.1.1. Synthesis

Addition of a lithium compound to a halovinylsilane followed by lithium halide elimination is one of the most convenient routes to silenes:

$$R_2Si(X)CH{=}CH_2 + R'Li \longrightarrow R_2Si(X)CH(Li)CH_2R' \xrightarrow[-LiX]{} R_2Si{=}CHCH_2R' \qquad (2)$$

Since the first reaction of this type described by Jones and Lim in 1977, probably leading to the unstable silene [$Me_2Si{=}CHCH_2{}^tBu$] [8], many other transient neopentylsilenes [$RR'Si{=}CHCH_2{}^tBu$] have been synthesized by this route, particularly by Auner and coworkers [10–22], but also some other authors [23,24] and us [25]. Despite the use of more and more bulky substituents, all these silenes are unstable at room temperature and lead to dimeric 1,3-disilacyclobutanes (head-to-tail dimerization):



(3)

Dimesitylneopentylsilene **1**, prepared in our group, is up to now the sole stable silene in the neopentyl series [48,49]. The precursor of **1** is fluoro(dimesityl)vinylsilane **2** obtained by hydrosilylation reaction between fluorodimesitylsilane and acetylene using hexachloroplatinic acid as catalyst:

$$Mes_2Si(F)H + HC{\equiv}CH \xrightarrow[C_6H_6]{H_2PtCl_6} \underset{\mathbf{2}}{Mes_2Si(F)CH{=}CH_2} \qquad (4)$$

1 is then obtained by addition of an equimolar quantity of tert-butyllithium in pentane at −78 °C. The addition is rapid and the elimination of lithium fluoride needs only a few minutes at room temperature:

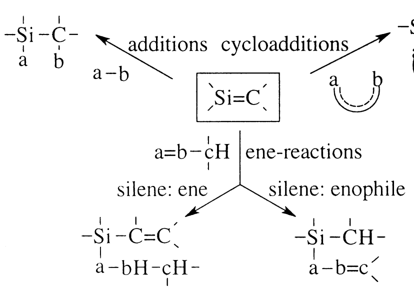
$$\mathbf{2} + tBuLi \xrightarrow[-78^\circ C]{pentane} Mes_2Si(F)CH(Li)CH_2tBu \xrightarrow[20^\circ C]{-LiF} \underset{\mathbf{1}}{Mes_2Si{=}CH\text{-}CH_2tBu} \qquad (5)$$

The silene **1** can be isolated as yellow crystals and shows characteristic NMR spectra: in the ^1H NMR spectrum we observed a triplet at 5.52 ppm for the ethylenic proton, in the ^{13}C NMR spectrum a signal at 110.4 ppm for the ethylenic carbon and in the ^{29}Si spectrum a low field signal at +77.6 ppm for the silicon atom.

Yellow pentanic solutions of **1** can be stored for some weeks under an inert atmosphere. They can be titrated and used with the same facility as a lithium compound or a Grignard reagent.

2.1.2. Reactivity

Despite its stability, **1** presents a high reactivity in the field of classical chemistry of silenes such as additions and cycloadditions but also, more originally, a versatile behaviour as ene or enophile reagent depending on the reactants. The reactivity of **1** [49] is summarized in Eq. (6):



(6)

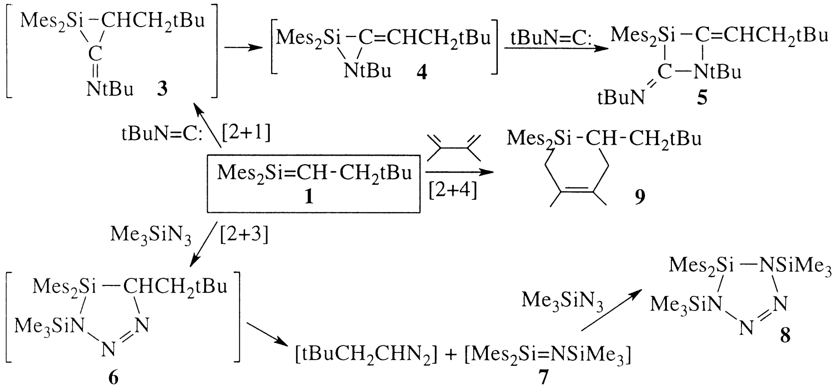
2.1.2.1. Addition reactions. Easy electrophilic or nucleophilic additions can be performed from **1** and various reactants such as water, alcohols and mineral acids [49]:

$$\underset{\mathbf{1}}{\mathrm{Mes_2Si{=}CH{-}CH_2tBu}} + \mathrm{A{-}H} \rightarrow \underset{\mathrm{A\,=\,OH,\ nBuO,\ F\ ...}}{\mathrm{Mes_2Si(A){-}CH_2CH_2tBu}} \qquad (7)$$

All these reactions are regiospecific in agreement with the well-established polarity $\mathrm{Si}^{\delta+}{=}\mathrm{C}^{\delta-}$ of the silicon–carbon double bond.

2.1.2.2. Cycloaddition reactions. Organometallic alkenes are well-known to give easy, often nucleophilic, cycloaddition reactions. The participation of the lone pairs of heteroatoms of the reactants in the initial step seems likely in most of these reactions.

A large range of cycloaddition reactions has been performed from **1** and isonitriles ([2+1]), azides ([2+3]) and dienes ([2+4]):



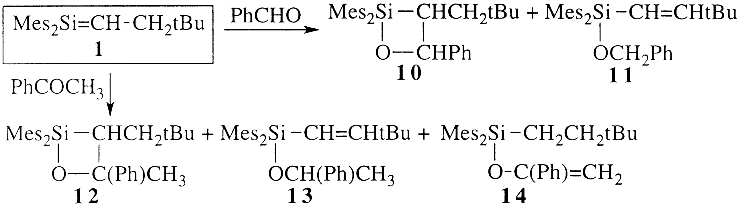
(8)

In the case of tert-butylisonitrile, only **5** was isolated [49]. However, we can postulate the initial formation of the silirane **3**, followed by a rearrangement leading to the silaaziridine **4** and by the insertion into the Si–N bond of a second equivalent of isonitrile. These results are in agreement with a theoretical study about the mechanism of the reaction between HN=C: and $H_2Si{=}CH_2$ [50] which predicted the silaaziridine with an exocyclic C=C bond (analogue to **4**) to be the most stable isomer. A rather similar reaction has been observed by Brook and coworkers from another silene [51,52].

With trimethylsilylazide, the formation of the silatetrazole **8** can be explained by a [5]→[2+3] decomposition of the cycloadduct **6** and a subsequent [2+3] cycloaddition between the transient silaimine **7** and trimethylsilylazide [49]. Similar sila- or germatetrazoles [53–55] have been obtained by Wiberg and coworkers from transient silenes or germenes.

A nearly quantitative Diels–Alder reaction was observed between **1** and 2,3-dimethylbutadiene, leading to the six-membered ring compound **9** [49]. Depending on the silene and on the diene, similar [2+4] cycloadditions, but also [2+2] cycloadditions and ene-reactions, have been reported [17,56–67].

With aldehydes and ketones, [2+2] cycloadditions are observed leading respectively to **10** and **12** [49]. However, these reactions are more complex since ene-reactions also occur giving **11**, **13** and **14**:



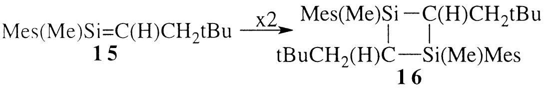
$$\boxed{\begin{array}{c}\text{Mes}_2\text{Si=CH-CH}_2\text{tBu}\\ \mathbf{1}\end{array}} \xrightarrow{\text{PhCHO}} \begin{array}{c}\text{Mes}_2\text{Si}-\text{CHCH}_2\text{tBu}\\ |\qquad |\\ \text{O}-\text{CHPh}\\ \mathbf{10}\end{array} + \begin{array}{c}\text{Mes}_2\text{Si}-\text{CH=CHtBu}\\ |\\ \text{OCH}_2\text{Ph}\\ \mathbf{11}\end{array}$$

$$\downarrow \text{PhCOCH}_3$$

$$\begin{array}{c}\text{Mes}_2\text{Si}-\text{CHCH}_2\text{tBu}\\ |\qquad |\\ \text{O}-\text{C(Ph)CH}_3\\ \mathbf{12}\end{array} + \begin{array}{c}\text{Mes}_2\text{Si}-\text{CH=CHtBu}\\ |\\ \text{OCH(Ph)CH}_3\\ \mathbf{13}\end{array} + \begin{array}{c}\text{Mes}_2\text{Si}-\text{CH}_2\text{CH}_2\text{tBu}\\ |\\ \text{O-C(Ph)=CH}_2\\ \mathbf{14}\end{array} \qquad (9)$$

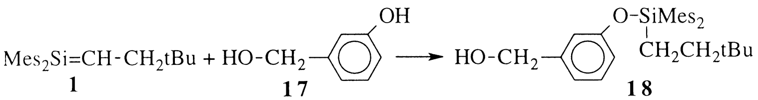
With benzaldehyde, the cycloadduct **10** is the major compound (75%) [49]. With acetophenone we have observed the formation of two types of ene-compounds **13** and **14**: **13** is analogous to the derivative **11** obtained with benzaldehyde (silene behaving as ene reagent), but **14** is formed by a reaction in which the silene **1** acts as enophile [49].

The stabilization of silenes is extremely dependent on the steric hindrance around the Si=C double bond since a slight change in the size of substituents drastically affects their stability. For example, silene Mes(Me)Si=CHCH$_2{}^t$Bu [25] has been prepared similarly to **1**, and dimerizes immediately at low temperature (−50 °C) to form the 1,3-disilacyclobutane **16** [25]:



$$\begin{array}{c}\text{Mes(Me)Si=C(H)CH}_2\text{tBu}\\ \mathbf{15}\end{array} \xrightarrow{\text{x2}} \begin{array}{c}\text{Mes(Me)Si}-\text{C(H)CH}_2\text{tBu}\\ |\qquad |\\ \text{tBuCH}_2\text{(H)C}-\text{Si(Me)Mes}\\ \mathbf{16}\end{array} \qquad (10)$$

The synthesis and the study of the chemistry of **1** prove the great interest of such organometallic alkenes: easy preparation in a large scale, good stability for a long time, high classical reactivity of silenes and original behaviour of ene or enophile reagent. Another interest of the silene **1** could be its use to protect acidic function in organic synthesis since it allows easy and fast introduction of a very bulky silyl group. Moreover, our first experiments [68] showed a very interesting selective protection of the more acidic function: for example one equivalent of **1** reacts only with the phenol function of **17** to give **18** leaving unaffected the alcohol moiety:



1 **17** **18** (11)

2.2. Germenes

Germenes $R_2Ge{=}CR'_2$ have been by far less studied than silenes.

Dimesitylfluorenylidenegermene $Mes_2Ge{=}CR_2$ (CR_2 = fluorenylidene) [6], isolated in 1987 by us, was the first example of a stable derivative with a formal germanium carbon double bond. At the same time [4,5] and more recently [69,70] some other stable germenes have been described.

2.2.1. Synthesis

An addition–elimination reaction as in silicon chemistry can be carried out to synthesize a stable germene [71]. This was performed from the fluorovinylgermane $Mes_2Ge(F)CH{=}CH_2$ **19**. The use of fluorine as leaving group limits the side reactions often observed in the case of chloro derivatives: because of the strong germanium–fluorine bond energy (114 kcal/mol [72]) a lithium/fluorine exchange does not occur with fluorogermanes. Fluorodimesitylvinylgermane **19** was prepared in one step from vinylmagnesium bromide and difluorodimesitylgermane:

$$\mathrm{Mes_2GeF_2 + CH_2{=}CH\text{-}MgBr \xrightarrow{THF} \underset{\mathbf{19}}{Mes_2Ge(F)CH{=}CH_2}} \tag{12}$$

Subsequent addition to **19** of a molar equivalent of tert-butyllithium at −78 °C gave the α-lithiogermane **20**; the elimination of lithium fluoride occurred at −50 °C with the nearly quantitative formation of dimesitylneopentylgermene **21**:

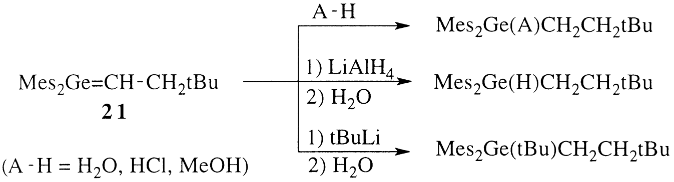
$$\mathbf{19} \xrightarrow[\mathrm{Et_2O/\text{-}78^\circ\,C}]{\mathrm{tBuLi}} \underset{\mathbf{20}}{\mathrm{Mes_2Ge(F)CH(Li)CH_2tBu}} \xrightarrow[\mathrm{-LiF}]{\mathrm{-50^\circ\,C}} \underset{\mathbf{21}}{\mathrm{Mes_2Ge{=}CH\text{-}CH_2tBu}} \tag{13}$$

21 can be isolated as yellow crystals and analysed by NMR spectroscopy. It showed the expected characteristic signals, both in the ^1H spectrum (two unequivalent mesityl signals and a triplet for ethylenic proton at 6.10 ppm) and in the ^{13}C spectrum (doubly bonded carbon at 124.2 ppm) [71].

Yellow solutions of germene **21** are stable at room temperature for a long time under inert atmosphere.

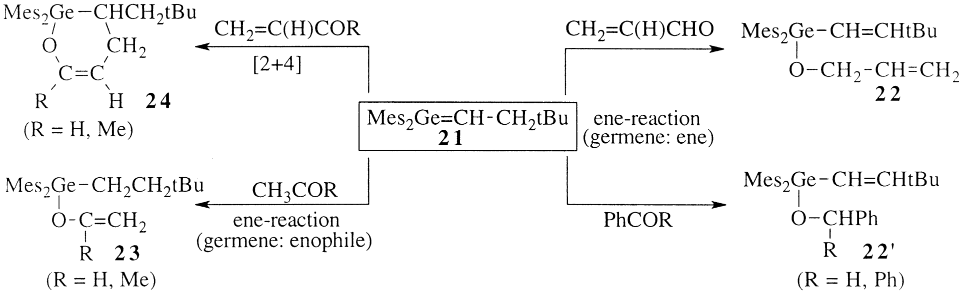
2.2.2. Reactivity

Despite its good thermal stability, **21** is highly reactive, particularly toward electrophilic or nucleophilic reagents (H_2O, HCl, MeOH, ^tBuLi, $LiAlH_4$) [73]:



(14)

By contrast with other stable germenes, **21** presents a lower steric hindrance around the doubly bonded carbon and has allylic hydrogens. Thus, as in the case of its silene isologue, the reactivity of **21** toward carbonyl compounds is of particular interest since **21** gives a wide range of reactions which are very dependent on the carbonyl compounds [73]; the results are summarized in Eq. (15):



(15)

Thus, with benzaldehyde and benzophenone, the germene **21** behaves as ene [73]; these reactions are stereoselective with the sole formation of the *E* isomer **22′**, probably for steric reasons. Such ene behaviour is very rare for an organometallic alkene since it has only been observed with the silene **1**; some other silenes generated by photolysis gave the same results but with a radical pathway [74–76].

The germene **21** reacts with acroleine both as ene and by a [2+4] cycloaddition in the ratio 50/50 [73] while only a [2+4] cycloaddition was observed with methyl vinyl ketone. As expected, **21** behaves as enophile with enolisable aldehydes and ketones such as ethanal and propanone [73]. Note that in the case of **23**, in contrast to **43** [Eq. (24)], no germanotropic rearrangement [77–79] is observed.

These results confirm once more the synthetic potential of such a type of organometallic alkenes having allylic hydrogens.

3. Substitution–elimination reactions

3.1. Germenes

3.1.1. Synthesis

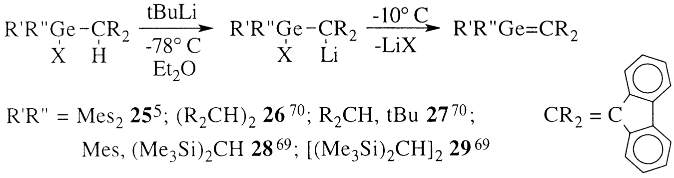
Dehydrohalogenation reactions of halofluorenylgermanes with tert-butyllithium allowed the synthesis of five stable germenes [6,69,70].

The use of fluorenylidene moiety presents two advantages:

- to allow a conjugation with the Ge=C double bond (see the paragraph devoted to X-ray structure) which could afford an additional amount of stabilization (although it is well-known that the main stabilizing effect for doubly bonded heavy elements of Group 14 is due to steric effect, the electronic effects are not completely negligible);

– another advantage of the fluorenyl group in the precursor is the presence of an acidic hydrogen easy to substitute by lithium. Note that the fluorenylidene group allowed the stabilization of other doubly bonded derivatives such as two phosphaalkenes –P=C⟨ [80] or a boraalkene –B=C⟨ [81].

The best yield in the dehydrohalogenation by a lithium compound was obtained when germanium was substituted by a fluorine; with a chlorine some side reactions (particularly a reduction of the Ge–Cl bond) are sometimes observed. However, in the case of difluorenyl or trifluorenyl derivatives, due to the very low solubility of the corresponding fluorogermanes, their chloro isologues should be preferred as precursor. Tert-butyllithium appeared as the best lithio compound: owing to the large size of ^{t}Bu, direct alkylation of germanium did not occur:



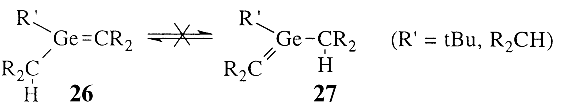
$R'R''Ge(X)-CR_2H \xrightarrow[-78°C,\ Et_2O]{tBuLi} R'R''Ge(X)-CR_2Li \xrightarrow[-LiX]{-10°C} R'R''Ge{=}CR_2$

R'R'' = Mes_2 **25**[5]; $(R_2CH)_2$ **26**[70]; R_2CH, tBu **27**[70]; Mes, $(Me_3Si)_2CH$ **28**[69]; $[(Me_3Si)_2CH]_2$ **29**[69]

(16)

The germene **25** presents an interesting thermochromism: it is yellow at −100 °C, orange at room temperature and orange–red at +80 °C.

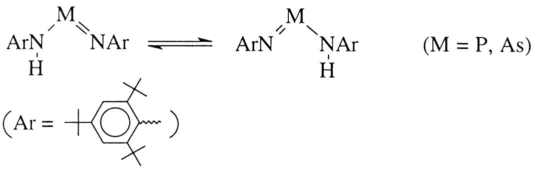
In germenes **26** and **27**, a prototropic effect between the fluorenyl and fluorenylidene groups which could be postulated, has not yet been observed:



26 **27**

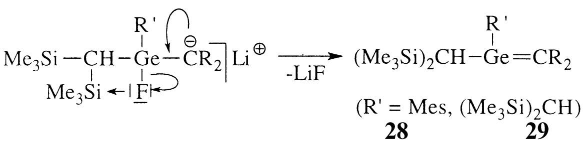
(17)

Such a prototropic effect has been demonstrated by Lappert and coworkers in the case of phospha- (or arsa-) imines [82]:



(18)

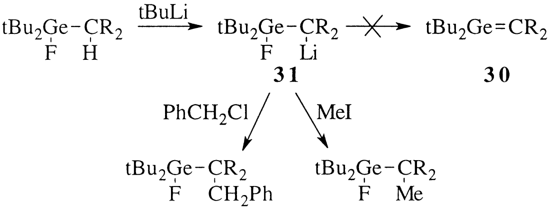
With one or two bis(trimethylsilyl)methyl groups on germanium, the easy formation of the germenes **28** and **29** from their lithium precursors could be partly caused by an electrophilic assistance of silicon by interaction with fluorine [69]:



28 **29**

(19)

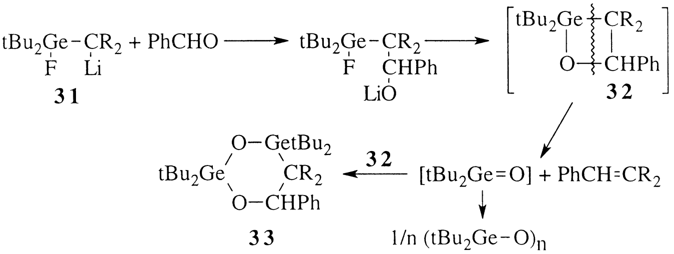
Attempts to prepare the germene **30** substituted on germanium by two tert-butyl groups failed [69]. Even by using various solvents (Et_2O, THF, pentane) or by heating, the elimination of lithium fluoride from **31** was unsuccessful. **31** was unambiguously characterized by quenching with methyl iodide or benzylchloride:



(20)

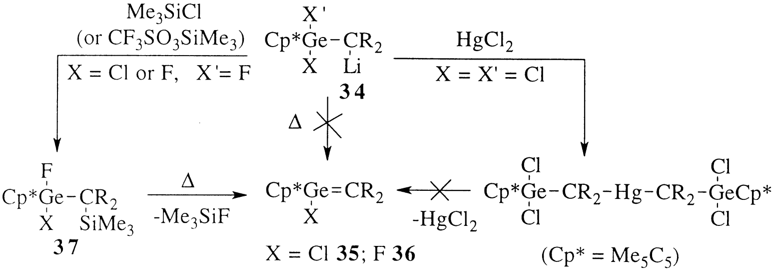
Therefore, there is a great difference in the chemical behaviour of Ge(F)–C(Li) compounds depending on the groups on germanium since with at least one aromatic group (mesityl) the elimination of LiF occurs below 0 °C. In the synthesis of germaphosphenes $\rangle$Ge=P–, a similar easier elimination of LiF was observed from $Mes_2Ge(F)P(Li)Ar$ [83] than from $^tBu_2Ge(F)P(Li)Ar$ [84]: rapid at −40 °C instead of 24 h at room temperature.

However, the lithium compound **31** behaves, at least in some cases, as a synthetic equivalent of the germene $^tBu_2Ge{=}CR_2$ **30**. **31** reacts with benzaldehyde to give the final six-membered ring compound **33** probably via the initially formed four-membered ring derivative **32**, which would be found also in a classical [2+2] cycloaddition between the germene **30** and benzaldehyde [69]:



(21)

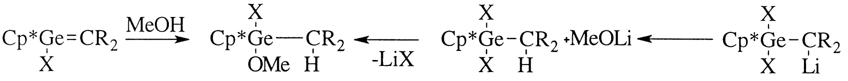
A similar high stability of a lithium salt has been observed in **34** [85]: elimination of lithium chloride or fluoride was impossible by heating or by addition of mercuric chloride. However, the halogermenes **35** and **36** could be obtained from **37** (prepared from **34** and Me_3SiCl or $CF_3SO_3SiMe_3$) by taking advantage of the lability of the silicon–fluorenyl bond and of the great energy of the silicon–fluorine bond, to eliminate Me_3SiF:



(22)

Such halogermenes have not yet been isolated but have been characterized by trapping reactions [85] [see Eqs. (23) and (25)]; they represent the first germenes substituted on germanium by a halogen, that should allow their functionalization. Moreover, the presence of the labile pentamethylcyclopentadienyl group offers a second possibility of functionalization since such a group, very often used by Jutzi and coworkers [86–88], is both a high stabilizing and a good leaving group.

However, like **31**, **34** can be considered as a synthetic equivalent of the halogermenes **35** and **36** since the reaction with methanol gives the same adduct as the one expected from the germenes:



$$\underset{X}{Cp^*Ge}{=}CR_2 \xrightarrow{MeOH} Cp^*\overset{X}{\underset{OMe}{Ge}}{-}\underset{H}{CR_2} \xleftarrow[-LiX]{} Cp^*\overset{X}{\underset{X}{Ge}}{-}\underset{H}{CR_2}\cdot MeOLi \longleftarrow Cp^*\overset{X}{\underset{X}{Ge}}{-}\underset{Li}{CR_2} \tag{23}$$

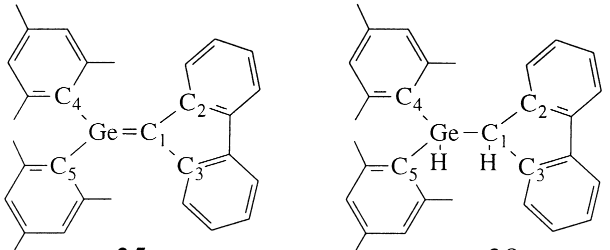
35, **36** **34**

3.1.2. *Physicochemical studies*

3.1.2.1. X-ray structure. The X-ray structure of **25** and also of the corresponding germane **38** (obtained by reduction of the Ge=C double bond by $LiAlH_4$) have been performed by Dräger and coworkers in order to have a comparison between two compounds substituted both on germanium and carbon by the same groups [89] (Scheme 2).

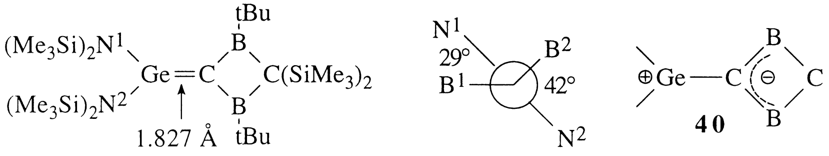
A shortening of about 0.18 Å was observed in the Ge=C double bond length (1.80 Å) in relation to the standard Ge–C single bond which is generally close to 1.98 Å [90,91]. However, the shortening is in fact more important since, due to the large steric hindrance, the Ge–C single bond in the corresponding germane **38** is elongated to 2.01 Å. Thus, the real shortening observed is about 10.5%, rather comparable to the shortening of the C–C bond between $(sp^3)C–C(sp^3)$ and $(sp^2)C=C(sp^2)$. The observed double bond length is in good agreement with calculations which predict values close to 1.78–1.80 Å [92].

A very interesting feature of the germene **25** is the shortening (0.04 Å) observed for the C_1C_2 and C_1C_3 bonds in relation to the corresponding bonds in the germane **38** (Scheme 2) [89] comparable to the one observed in the central C–C bond of dienes [93]. Therefore there is, as expected, significant conjugation between the



25 **38**

Scheme 2.



39

40

Scheme 3.

Ge=C double bond and the fluorenylidene group. Consequently the germene 25 could theoretically behave as a germadiene, which experimentally occurs in the reaction with phosphaalkyne $^tBuC{\equiv}P$ [see Eq. (37)].

The torsion angle between the two planes $C_1C_2C_3$ and GeC_4C_5 is very small: 5.9° [89]. Much larger torsion angles (29 and 42°) were observed in the germene **39** [4,5] synthesized by Berndt and coworkers by a very nice coupling reaction between a carbene and a germylene (Scheme 3).

These results confirm the importance of the ylide resonance form **40**; however, such an ylide structure, to some extent, should also occur in the germene **25** with the negative charge being delocalized on the fluorenylidene group.

The bond order in **25** is significantly less important than in the parent compound $H_2Ge{=}CH_2$: 1.50 versus 1.81 [89]. The dipole moment was estimated to be 4 Debye [89].

3.1.2.2. ^{13}C NMR and Raman spectra. The germene **27** was characterized in ^{13}C NMR by a signal at 79.3 ppm for the carbon doubly bonded to germanium [70]. Similar low field shifts were reported by Berndt and coworkers in germenes in which the doubly bonded carbon is substituted by two boron atoms [4,5] (115 ppm for **39** and 93 ppm for another germene with a similar structure).

The Raman Ge=C valence vibration has been determined for the germene **25** by comparison with the Raman spectrum of the corresponding germane **38**. The only significant difference between the two spectra was a marked emission at 988 cm^{-1} attributed to the Ge=C vibration [89]. Ab initio SCF and MNDO calculations gave respectively 906 [92] and 854 cm^{-1} [89] for $H_2Ge{=}CH_2$ and MNDO calculations gave 1018 cm^{-1} [89] for $Mes_2Ge{=}CR_2$.

3.1.2.3. Theoretical studies. The π-bond energies of $\rangle M{=}C\langle$ (M = C, Si, Ge, Sn) compounds decrease from C to Sn (Table 1).

However, if there is a great difference between alkenes and their heavier analogues, silenes and germenes have similar π-bond energies and should present, as experimentally observed, about the same stability.

In the series of $GeCH_4$ compounds, methylgermylene is the most stable species and germylmethylene the least stable as determined by an ab initio quantum-mechanical method [96] (Scheme 4).

Other theoretical studies predicted a slightly larger barrier [97] and exothermicities [92,97], probably due to less exhaustive incorporation of electron correlation effects.

$$\mathrm{H_3C{-}Ge(H){:}} \;>\; \underset{\substack{\uparrow \\ 11.4\ \text{kcal/mole}}}{\mathrm{H_2C{=}GeH_2}} \;>\; \mathrm{{:}C(H){-}GeH_3}$$

$$\text{isomerization enthalpy barrier: } 33.1\ \text{kcal/mole}$$

Scheme 4.

Table 1
π-Bond energies (kcal/mol) of >M=C< (M = C, Si, Ge, Sn)

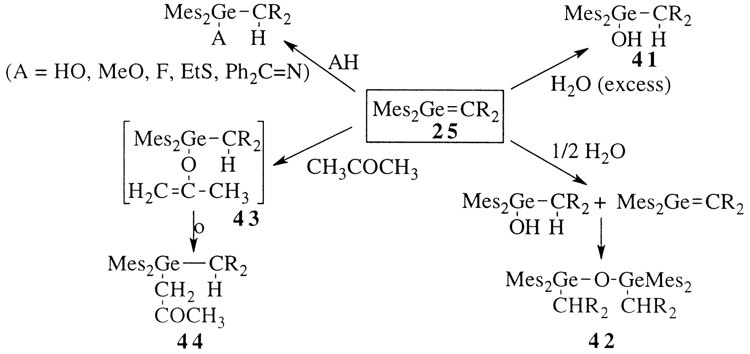
>C=C<	>Si=C<	>Ge=C<	>Sn=C<
64–68 [94]	35–36 [94]	31 [94] 32.2–33 [95]	19 [94] 20.9–21 [95]

A rather important polarity was calculated for the Ge=C double bond [92] in $H_2Ge{=}CH_2$: Ge +0.35, C −0.61, however, less than in the corresponding silene: Si +0.54, C −0.71.

3.1.3. Reactivity

Solutions of the germenes **25–29** are generally orange; they are extremely air- and moisture-sensitive: addition of minute amounts of oxygen immediately affords green solutions. However, the germenes **25–29** are thermally stable since no dimerization or decomposition was observed at room temperature in solution or even by heating. For example, dimesityl(fluorenylidene)germene $Mes_2Ge{=}CR_2$ **25**, which is the most thoroughly studied germene, was recovered unchanged after heating in a sealed tube at 120 °C during several days.

3.1.3.1. Additions to the Ge=C double bond. The germene **25** is extremely reactive toward protic reagents: alcohols, thiols, hydrofluoric acid, etc. add quantitatively to the Ge=C double bond [6]. Diphenylimine $Ph_2C{=}NH$ reacts only as protic reagent and never affords a [2+2] cycloadduct with the C=N double bond [98]:



(24)

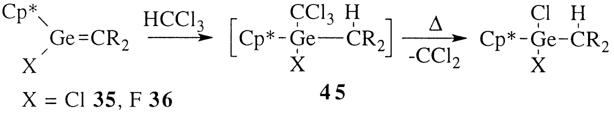
All the other fluorenylidenegermenes give a similar regiospecific addition of methanol to the Ge=C double bond [69,70]. Hydrochloric acid also reacts with the Ge–C unsaturation of the germene **39** [4,5].

Water gives two types of products: with an excess, the hydroxygermane **41** was obtained exclusively [99], whereas with only a half-equivalent, the digermoxane **42** was formed [99], probably by addition of the O–H bond of the hydroxygermane **41** to the Ge=C double bond of the unreacted germene [Eq. (24)].

Acetone reacts with **25** only as a protic reagent leading to the transient derivative **43** which undergoes a germanotropic rearrangement [77–79] to afford **44**.

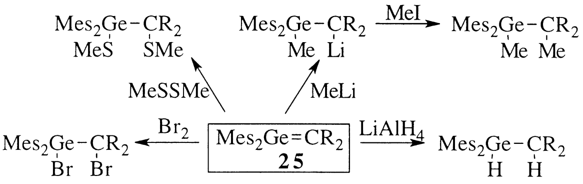
Note that with other main group derivatives, acetone reacts either as a protic reagent or gives [2+2] cycloadditions and sometimes both reactions depending on the Group 14 metal used and on its substituents. For example, with symmetrical M=M derivatives such as disilenes or digermenes substituted by four mesityl groups, only [2+2] cycloadditions occurred [100,101]. With silenes, only the reaction of acetone by its enolic form has been reported by Wiberg and Wagner [67] and with disilene $^tBu_2Si=Si^tBu_2$, both reactions are observed [102].

The chloro- and fluorogermenes **35** and **36** react with chloroform leading to the transient adducts **45** which lose dichlorocarbene in the conditions of the reaction [85]:



(25)

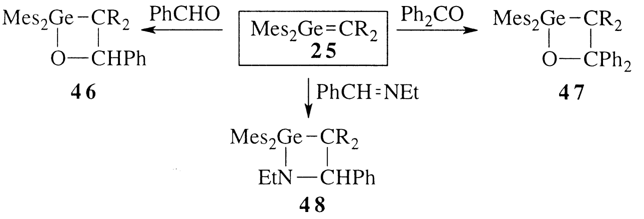
The germene **25** is also very reactive toward electrophiles, nucleophiles and in radical processes:



(26)

Thus, almost quantitative additions to the Ge=C double bond are observed with bromine [103], methyllithium (quenching with methyl iodide affords a new germane) [103], lithium aluminium hydride [6] (the reaction must be performed at 0 °C to avoid the cleavage of the Ge–fluorenyl bond) and dimethyldisulfide [6].

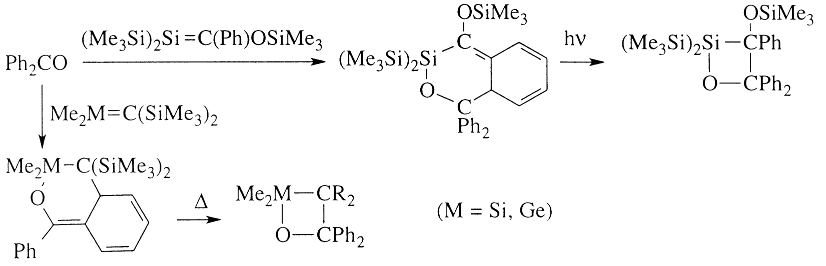
3.1.3.2. [2+2] Cycloadditions. Many types of cycloadditions have been observed from **25**: for example, [2+2] cycloadditions with non-enolisable aldehydes and ketones to give the four-membered ring compounds **46** and **47** [99]:



(27)

Such cycloadducts are very thermally stable and no decomposition by a [4]→[2+2] process, leading to the transient dimesitylgermanone $Mes_2Ge{=}O$ and the corresponding alkenes, neither a [2+2] cycloreversion, have been observed. Note that germaoxetanes with less bulky groups on germanium generally easily decompose by one of these processes [104–107]. The large steric hindrance caused by mesityl groups in **46** and **47** is clearly demonstrated by the X-ray structure which displays long Ge–fluorenyl bonds: 2.03 Å in **46** and even 2.07 Å in **47** [99], whereas normal Ge–C distances range from 1.90 to 1.98 Å [90,91]. It is also indicated in the ^1H NMR spectrum which shows hindered rotation of the mesityl groups (the free energy of activation for their rotation was calculated to be 13.8 kcal/mol) [99].

Other types of reactions have been reported by Wiberg or Brook between benzophenone and transient germenes or silenes:

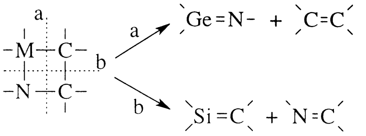


(28)

For example, with $Me_2M{=}C(SiMe_3)_2$ (M = Si, Ge) a [2+4] cycloaddition was first observed followed by a thermal isomerization to the four-membered ring compound [108,109]. A [2+4] cycloaddition was also observed by Brook et al. from $(Me_3Si)_2Si{=}C(Ph)OSiMe_3$ but involving in this case the phenyl group of the silene [110] [Eq. (28)].

N-ethylphenylimine also gives with **25** the [2+2] cycloadduct **48** but only after heating at 140 °C. Only one isomer was obtained, with phenyl and ethyl in trans [98] [Eq. (27)].

48 is the first thermally stable heterocycle of this type since germaazetidines obtained by other routes are generally unstable and are good precursors of germaimines: (route **a**) [111,112].



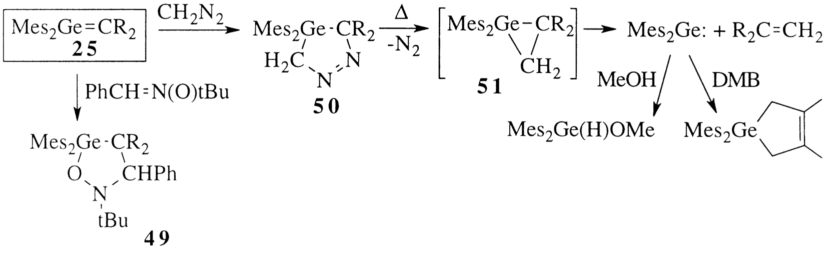
(29)

Note that, in contrast to germaazetidines, the silaazetidine isologues give only a cycloreversion leading to starting silenes and imines (route **b**) [113–116].

A [2+2] cycloaddition with nitrosobenzene was also observed [see Eq. (35)].

3.1.3.3. [2+3] Cycloadditions. N-(tert-butyl)-α-phenylnitrone and diazomethane give with **25** [2+3] cycloadditions leading to the five-membered heterocycles **49**

[6] and **50** [117,118]:

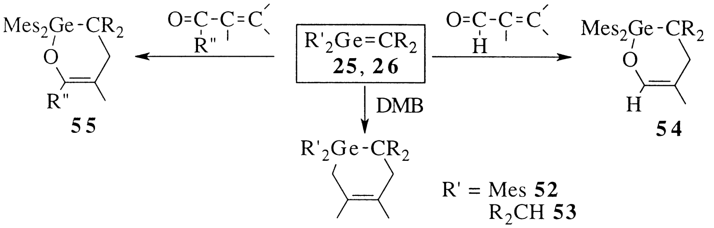


(30)

These two reactions are regiospecific. The germapyrazoline **50** is a good precursor of the germirane **51** at 60 °C. However, **51** is not stable and undergoes a [3]→[2+1] decomposition, with formation of the corresponding alkene and germylene which was characterized by trapping with methanol and dimethylbutadiene [117] [Eq. (30)].

Attempts to trap germirane were unsuccessful due to its short lifetime. Note that only two germiranes have been stabilized up to now owing to very large steric hindrance [119].

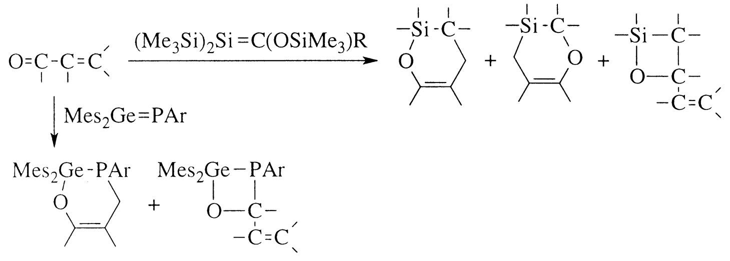
3.1.3.4. [2+4] Cycloadditions. [2+4] Cycloadditions occur from **25** and **26** and 2,3-dimethylbutadiene leading to **52** [6] and **53** respectively [70]:



(31)

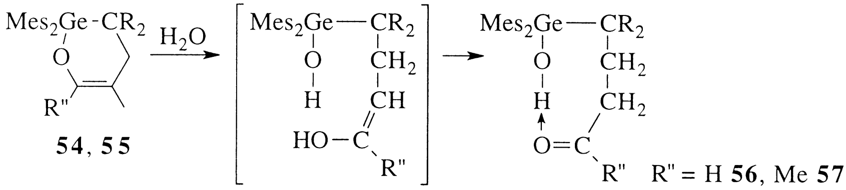
An ene reaction has never been observed.

Exclusive [2+4] cycloadditions occur between **25** and α,β-unsaturated aldehydes and ketones [120] with formation of **54** and **55**, whereas both [2+2] and [2+4] cycloaddition reactions are observed with other doubly bonded germanium compounds such as germaphosphenes [121] or with silenes [122]:



(32)

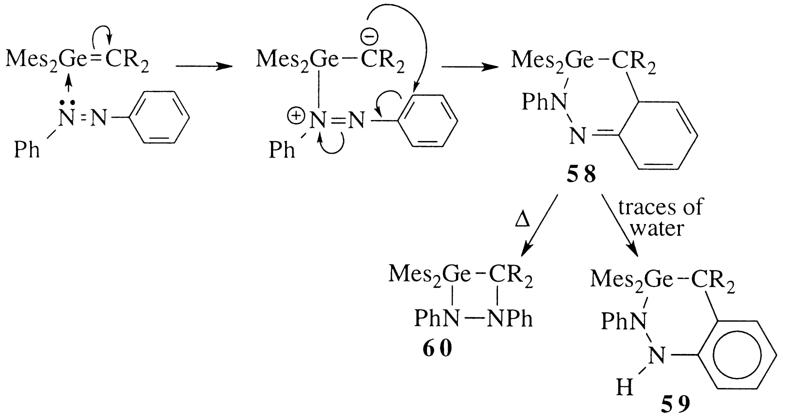
Hydrolysis of **54** and **55** leads respectively to new γ-germylated aldehydes or ketones **56** and **57** [120]:



(33)

The ^1H NMR spectrum of **57** shows very different chemical shifts for the methyl (1.10 ppm) and the methylene (3.31–3.49 ppm) groups bonded to the carbonyl group [120]: such a phenomenon is explained by a pseudocyclic structure due to a hydrogen bond leading to very different positions of these CH_3 and CH_2 toward the fluorenyl group.

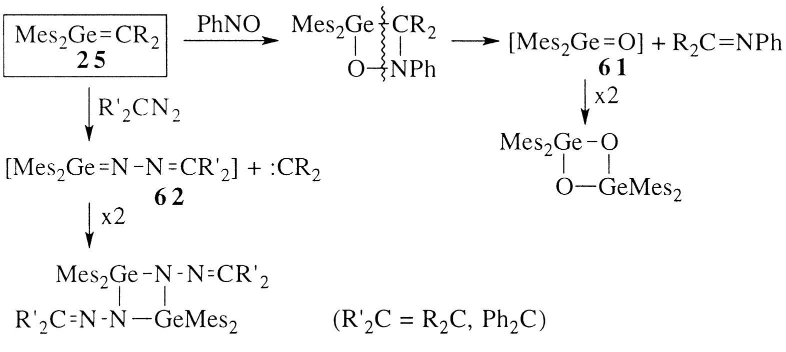
Between azobenzene and **25**, a [2+4] cycloaddition also occurred involving both the N=N double bond and a carbon–carbon bond of the phenyl group [98]:



(34)

Isomerization of the cycloadduct **58** to **59** by traces of water or to the four-membered ring **60** by thermolysis was observed [98].

3.1.3.5. Germenes as precursors of other doubly bonded germanium derivatives. Derivatives with $\rangle Ge{=}O$ double bond (germanones) or $\rangle Ge{=}N{-}$ double bond (germaimines) can be obtained from the germene **25** and nitrosobenzene, diphenyldiazomethane or diazofluorene:

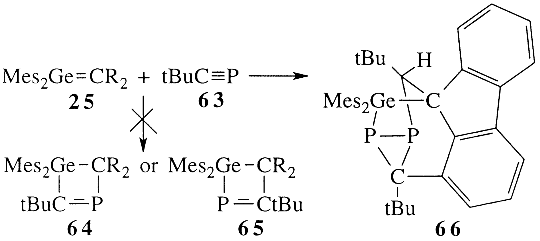


(35)

The germanone **61** [98] and germaimine **62** [123] normally lead to their dimer.

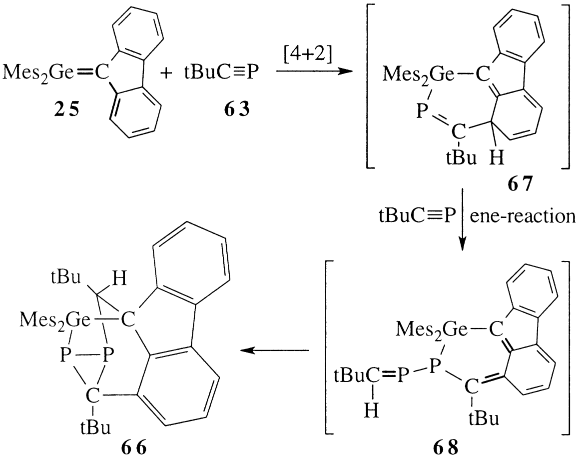
Similar reactions performed from more sterically hindered germenes should lead to stable germanones and germaimines.

3.1.3.6. Diene behaviour of the germene ***25***. Between the germene **25** and tert-butylphosphaalkyne **63**, [2+2] cycloadducts **64** or **65**, depending on the regiochemistry, were supposed to be formed. But the reaction was completely different from expected, giving surprisingly the polycyclic derivative **66** [124]:



(36)

The mechanism leading to **66** involves in the first step a Diels–Alder reaction in which the germene **25** reacts as a 1,3-diene with participation of one aromatic carbon–carbon bond of the fluorenylidene group:



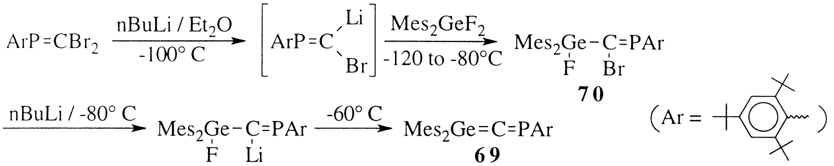
(37)

This cycloaddition step is followed by an ene reaction of **67** with a second equivalent of **63** acting as an enophile, which affords **68**. The latter species undergoes an intramolecular Diels–Alder reaction to give the final product **66**.

As said previously, the 1,3-diene behaviour of **25** is not surprising from its crystal structure which reveals shortened C_1–C_2 and C_1–C_3 bonds (see Scheme 2) due to a diene-typical conjugation between the Ge=C double bond and one aromatic carbon–carbon bond [89].

3.2. Germaphosphaallenes

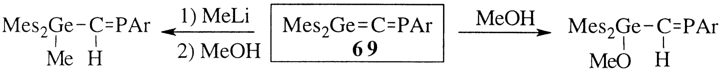
The first germaphosphaallene **69** $Mes_2Ge{=}C{=}PAr$ was recently obtained in our group [125]. Of course this compound is not a germene, but a "heavy allene" and not a "heavy alkene". However, as it has a Ge=C double bond, we can mention it and briefly describe its synthesis and reactivity. **69** has been obtained by debromofluorination of the corresponding fluorogermylphosphaalkene **70** according to the following reaction process:



(38)

69 was easily characterized by low field shifts in ^{31}P NMR (+240 ppm) and ^{13}C NMR (+280.9 ppm, $^1J_{CP}=75.1$ Hz) for the allenic carbon.

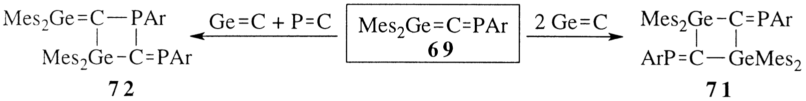
69 is stable only between −60 and −40 °C and is very reactive at −40 °C toward methyllithium and methanol which add to the Ge=C double bond:



$$\underset{Me\quad H}{Mes_2Ge{-}C{=}PAr} \xleftarrow[2)\ MeOH]{1)\ MeLi} \boxed{\underset{\mathbf{69}}{Mes_2Ge{=}C{=}PAr}} \xrightarrow{MeOH} \underset{MeO\quad H}{Mes_2Ge{-}C{=}PAr} \qquad (39)$$

Additions to the P=C double bond have never been observed [125].

In the absence of trapping reagents, it gives two types of dimers: the expected head-to-tail dimer **71** (dimerization between two Ge=C bonds) and the unexpected dimer **72** (dimerization between a Ge=C and a P=C bonds):



$$\underset{\mathbf{72}}{\begin{matrix} Mes_2Ge{=}C{-}PAr \\ Mes_2Ge{-}C{=}PAr \end{matrix}} \xleftarrow{Ge{=}C\ +\ P{=}C} \boxed{\underset{\mathbf{69}}{Mes_2Ge{=}C{=}PAr}} \xrightarrow{2\ Ge{=}C} \underset{\mathbf{71}}{\begin{matrix} Mes_2Ge{-}C{=}PAr \\ ArP{=}C{-}GeMes_2 \end{matrix}} \qquad (40)$$

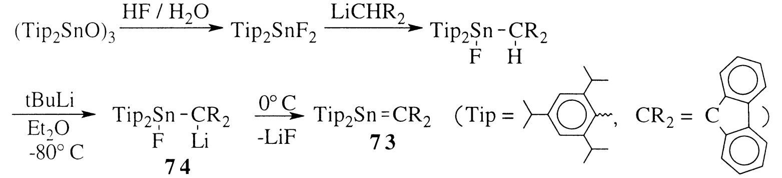
A similar behaviour was observed for ketenes with cycloadditions between two C=C bonds or between one C=C and one C=O bonds [126,127]. The type of dimerization in X=C=P compounds is very dependent on the nature of X as observed with X=O [128], S [129], NR [130].

Preliminary calculations have been performed on model dimers of parent $H_2Ge{=}C{=}PH$ [125]. However, a few discrepancies with the experiment are observed due to the use in calculations of H instead of extremely bulky groups (Ar and Mes).

3.3. Stannenes

3.3.1. Synthesis

The dehydrofluorination reaction, very successful for the synthesis of germenes, was also a good route to a compound with a tin–carbon double bond, the bis[(2,4,6-triisopropyl)phenyl]fluorenylidenestannene $Tip_2Sn{=}CR_2$ **73** [131]; **73** was obtained from $(Tip_2SnO)_3$, previously described by Masamune and Sita [132], by the following process:



(41)

The reaction between ^{t}BuLi and fluorostannane $Tip_2Sn(F)–C(H)R_2$ was followed by ^{119}Sn NMR between $-80\,°C$ and room temperature which allowed the characterization of the lithium compound intermediate **74** ($\delta^{119}Sn = +9.8$ ppm, $^1J_{SnF} = 1999$ Hz). The elimination of lithium fluoride was observed at 0 °C, leading to a deep violet solution of the expected stannene.

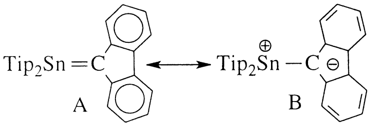
3.3.2. Physicochemical studies

73 was evidenced by a low field shift in ^{119}Sn NMR spectrum at +288 ppm, characteristic of a doubly bonded tin, since other stannenes give signals in this range: from +374 [133] to 647 [7], 710 [134] and 835 [7]. The only exceptions are a stannene substituted by two chlorines which gives a signal at −59.4 ppm [135] and the stannaketenimine $R_2Sn{=}C{=}NMes$ [136] [$R = 2,4,6\text{-}(CF_3)_3C_6H_2$] with a signal at very high field (−150 ppm).

However, the stannene **73** is at the lower limit for the chemical shift of a stannene. This can be explained by a complexation of tin by Et_2O as evidenced by ^1H NMR (broad signals for the OCH_2 protons of one Et_2O molecule). By addition of THF, signals of Et_2O become sharper whereas those of THF broaden, proving a complexation of tin by THF. However, the ^{119}Sn chemical shift is still about the same (287.3 ppm). Such complexation by weak Lewis bases has already been reported in silenes [137] and germenes [6], which have an electrophilic metal centre with a rather polarized double bond $Si^{\delta+}{=}C^{\delta-}$ or $Ge^{\delta+}{=}C^{\delta-}$.

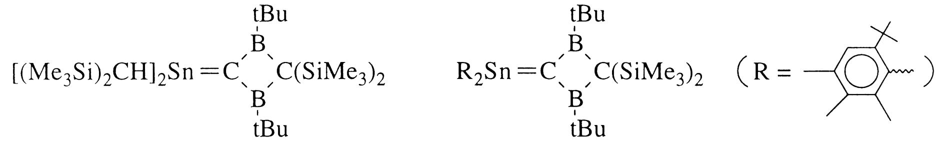
In UV, the stannene **73** presents an absorption at 542 nm ($\pi\rightarrow\pi^*$ transition of the $Sn{=}C$ double bond). **73** was also identified by its ^{13}C NMR spectrum which displays a signal at 133.85 ppm for the carbon doubly bonded to tin [131] (142 and 91 ppm for stannenes prepared by Berndt and coworkers [7]).

Like the germenes **25–29**, the stannene presents a marked polarity $Sn^{\delta+}{=}C^{\delta-}$. Thus, it seems possible to write two limiting forms A and B for **73**:



(42)

Unfortunately, it has not been possible to obtain suitable single crystals of **73** to perform an X-ray structure. Such crystallographic study on **75** [5,7] and **76** [133] (Scheme 5) shows a $Sn{=}C$ double bond length of respectively 2.025(4) Å and

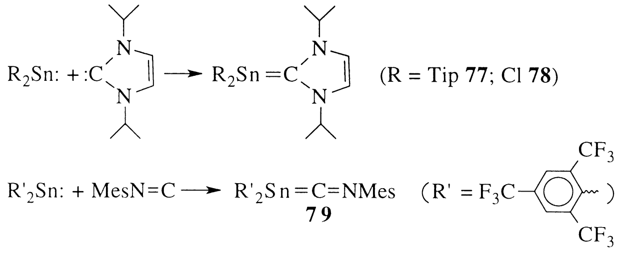


75 **76**

Scheme 5.

2.032(5) Å: the shortening is about 6% in relation to the standard Sn–C single bond and in agreement with the calculated bond length in $H_2Sn{=}CH_2$ (1.982 Å) [94]. The very large twist angle (61°) in **75** proves the contribution of an ylide form analogous to B. This twist angle is markedly less important (36°) in **76** [133].

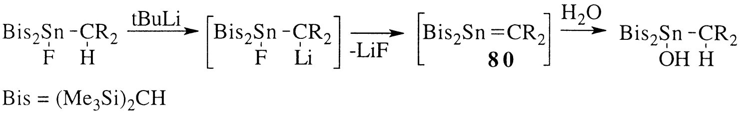
Note that other stannenes such as **77** and **78** and the stannaketenimine **79** obtained by reaction between a stannylene and an imidazole carbene [134, 135] or mesitylisocyanide [136] respectively present a much longer Sn–C double bond (2.290 [135], 2.379 [134] and 2.397 Å [136]) and a marked pyramidal tin:



(43)

The synthesis of stannene **73** was successful only in Et_2O or in a mixture of solvents such as toluene/Et_2O with at least 10% of Et_2O. In THF, the formation of **73** did not occur.

A transient stannene, the bis[bis(trimethylsilyl)methyl]fluorenylidenestannene **80**, was synthesized by a similar dehydrofluorination reaction [138]. However, it could not be stabilized, and was only evidenced by hydrolysis [138]:



$$\mathrm{Bis_2}\underset{\mathrm{F}}{\mathrm{Sn}}-\underset{\mathrm{H}}{\mathrm{CR_2}} \xrightarrow{\mathrm{tBuLi}} \left[\mathrm{Bis_2}\underset{\mathrm{F}}{\mathrm{Sn}}-\underset{\mathrm{Li}}{\mathrm{CR_2}}\right] \xrightarrow[\mathrm{-LiF}]{} \left[\underset{\mathbf{80}}{\mathrm{Bis_2Sn{=}CR_2}}\right] \xrightarrow{\mathrm{H_2O}} \mathrm{Bis_2}\underset{\mathrm{OH}}{\mathrm{Sn}}-\underset{\mathrm{H}}{\mathrm{CR_2}}$$

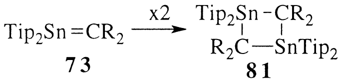
$\mathrm{Bis} = (Me_3Si)_2CH$

(44)

Thus, it appears once again that the use of aromatic groups on metal stabilizes the metal–carbon double bond.

3.3.3. *Reactivity of 73*

The stannene **73** is stable for a long period (at least one month) in solution at −25 °C. But at room temperature, it slowly dimerizes ($t_{1/2} \sim 1$ h) to form the head-to-tail dimer **81** [131,139]:

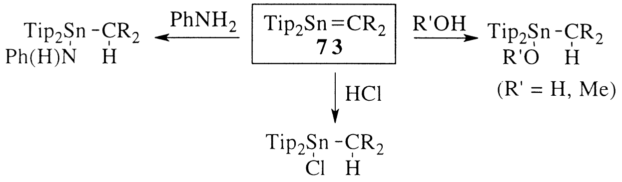


(45)

A similar type of dimerization is generally observed with silenes [34,35,39], germenes [44,45] and the transient stannene $Me_2Sn{=}C(SiMe_3)_2$ [140] which have a significantly polarized M=C double bond. Head-to-head dimerizations leading to 1,2-disilacyclobutanes [39] or disilanes [39] were only observed in silenes substituted on silicon by trimethylsilyl groups such as $(Me_3Si)_2Si{=}C(OSiMe_3)R$.

Only one 1,3-distannacyclobutane had previously been reported [140,141]; generally trimeric or tetrameric structures $(Sn–C)_n$ ($n=3$, 4) were obtained [142]. The four-membered ring **81** is planar with four nearly identical Sn–C bonds [2.288(4) to 2.293(5) Å] [139] which are significantly longer than the standard Sn–C bond (generally 2.14–2.18 Å [143–146]). Such bond lengths correspond to single bonds in sterically encumbered tin compounds [136,147]; shorter tin–carbon bonds in the range 2.17–2.20 Å are observed in a less crowded stannacyclobutane [148] or in a 1,2-distannacyclobutane [149].

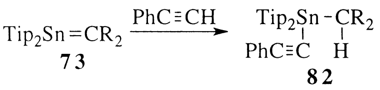
The stannene **73** is, as expected, extremely air- and moisture-sensitive; it reacts immediately with water [131,139], alcohols [139], aniline [139], hydrochloric acid [139] to give the corresponding regioisomers:



(46)

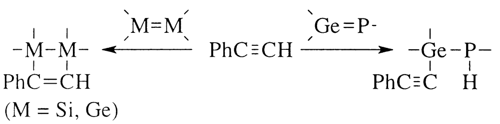
In such reactions with protic reagents only the bond reacts. By contrast, addition of tert-butyl alcohol to the stannaketenimine **79** leads to $(^tBuO)_2Sn$ by cleavage of the Sn–C single bonds [136].

Phenylacetylene reacts with **73** as a protic reagent to give **82** [139]:



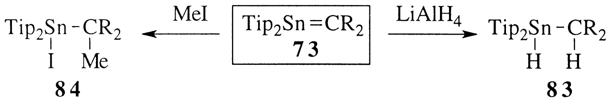
(47)

A similar reaction was observed with unsymmetrical M–M′ compounds like germaphosphenes [150], whereas [2+2] cycloadditions were observed with symmetrical M=M compounds such as digermenes [101,151] or disilenes [152]:



(48)

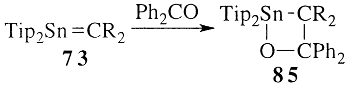
Reduction of the Sn=C double bond by $LiAlH_4$ as well as addition of methyl iodide also occur [139]:



$$\underset{\mathbf{84}}{\underset{\mathrm{I}\quad\mathrm{Me}}{\mathrm{Tip_2Sn{-}CR_2}}} \xleftarrow{\mathrm{MeI}} \boxed{\underset{\mathbf{73}}{\mathrm{Tip_2Sn{=}CR_2}}} \xrightarrow{\mathrm{LiAlH_4}} \underset{\mathbf{83}}{\underset{\mathrm{H}\quad\mathrm{H}}{\mathrm{Tip_2Sn{-}CR_2}}} \tag{49}$$

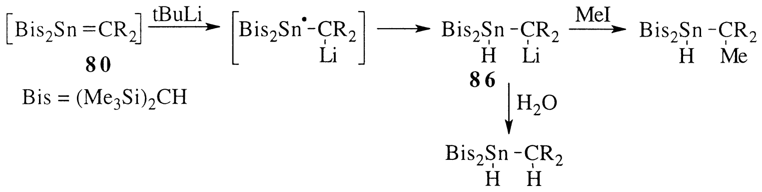
The latter reaction confirms the great reactivity of the Sn=C unsaturation; generally alkyl halides are not very reactive toward M_{14}=X compounds, since only an addition of methyl iodide to a Ge=N double bond has been reported [153].

The stannene **73** also reacts with benzophenone to give by a [2+2] cycloaddition the stable stannaoxetane **85** [154]:



$$\underset{\mathbf{73}}{\mathrm{Tip_2Sn{=}CR_2}} \xrightarrow{\mathrm{Ph_2CO}} \underset{\mathbf{85}}{\underset{\mathrm{O{-}CPh_2}}{\mathrm{Tip_2Sn{-}CR_2}}} \tag{50}$$

The transient stannene **80** reacts with ^{t}BuLi, probably by a single electron transfer reaction to lead, after abstraction of hydrogen from the solvent, to the lithium compound **86** which can be quenched by MeI or H_2O [138]:



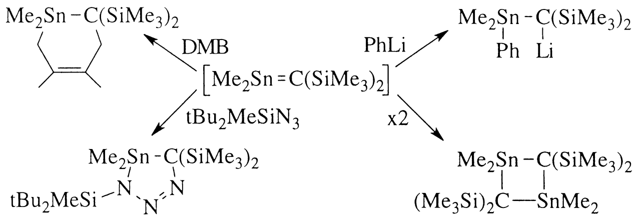
$$\underset{\mathbf{80}}{[\mathrm{Bis_2Sn{=}CR_2}]} \xrightarrow{\mathrm{tBuLi}} \left[\underset{\mathrm{Li}}{\mathrm{Bis_2Sn^{\bullet}{-}CR_2}}\right] \longrightarrow \underset{\mathbf{86}}{\underset{\mathrm{H}\quad\mathrm{Li}}{\mathrm{Bis_2Sn{-}CR_2}}} \xrightarrow{\mathrm{MeI}} \underset{\mathrm{H}\quad\mathrm{Me}}{\mathrm{Bis_2Sn{-}CR_2}}$$

$$\mathbf{86} \xrightarrow{\mathrm{H_2O}} \underset{\mathrm{H}\quad\mathrm{H}}{\mathrm{Bis_2Sn{-}CR_2}} \tag{51}$$

Bis = $(Me_3Si)_2CH$

By contrast, phenyllithium normally adds to the double bond of the less encumbered and transient $Me_2Sn{=}C(SiMe_3)_2$ [140].

Both [2+3] and [2+4] cycloadditions with azides and dimethylbutadiene, as well as a head-to-tail dimerization have also been reported [140] for this transient stannene:



(52)

The reactivity of stannenes is not yet very well-known, particularly by comparison with silenes and germenes. This is due to the great difficulty in obtaining stable stannenes and also in the purification of adducts: for example, in some cases the Sn–C single bond itself is cleaved in solution during the recrystallization and some rearrangements occur, whereas Si–C or Ge–C bonds are generally much stronger allowing easy purification of the adducts.

4. Conclusion

This review describes the French contribution to the impressive amount of results obtained in the field of metallaalkenes, after only 15 years of intensive research. Such compounds, which can be stabilized as monomers, mainly owing to a large steric hindrance, are much more reactive than the corresponding alkenes and appear as promising synthons in organic and organometallic chemistry. Polymers from these metallaalkenes would also probably be of great interest in applied chemistry as new materials. However, although compounds with a M=C double bond begin to be well-known, much research is still devoted to such derivatives as well as to new types of unsaturated species: they have already been successful for silaallenes $\rangle Si=C=C\langle$ by West and coworkers [155,156], a germaallene $\rangle Ge=C=C\langle$ by Okazaki and coworkers [157] and, as said previously, a germaphosphaallene $\rangle Ge=C=P–$ by us [125]. Various types of stable metalladienes and of triple-bond $–M\equiv C–$ or $–M\equiv M–$ compounds, still unknown, are the next targets.

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