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Recent developments in the chemistry of stable doubly bonded germanium compounds

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ABSTRACT

During the last 10 years, several compounds of the type Ge=X (X = C, Ge, N, P, S) have been isolated as monomers. The stabilization of such derivatives, which are generally highly polymerizable, was achieved by using very bulky groups both on the germanium atom and on the heteroelement X. Conjugation (particularly in a few germenes and germaimines) and intramolecular or intermolecular coordination with oxygen or nitrogen, also contributes, in some cases, to the stabilization. The X-ray analyses of such compounds show a significant bond shortening of the double bond (8–10%) relative to the corresponding single bond and a planar or nearly planar germanium. These doubly bonded germanium derivatives are usually thermally stable but must be handled in an inert atmosphere because of their high sensitivity to oxygen and moisture; they are extremely reactive, much more than the corresponding carbon analogues. Nearly quantitative additions on the double bond have been observed with electrophiles and nucleophiles, and various types of cycloadditions also occur. Except in one case, a germylene behavior has not been observed, proving that such compounds retain their structural integrity in solution.

A. INTRODUCTION

A large part of the richness of organic chemistry results from the ability of carbon to form double and triple bonds with itself or with other elements. So it seemed very promising to try to obtain similar multiply bonded species with heavier elements of Group 14, such as silicon, germanium and tin, and consequently to develop new heterocompounds. However, all attempts over a long time have been unsuccessful, leading exclusively to oligomers. The first evidence for transient M=X species (M = Si, Ge, Sn; X = C, O, S, N, P, Si, Ge, Sn) was obtained in the 1960s and 1970s with their in situ trapping [1a]. However, during the last 10 years, great progress has been made in the organometallic chemistry of Group 14 elements, with new synthetic routes to doubly bonded species and particularly with their stabilization due to substituents having large steric effects, and electronic effects in some cases.

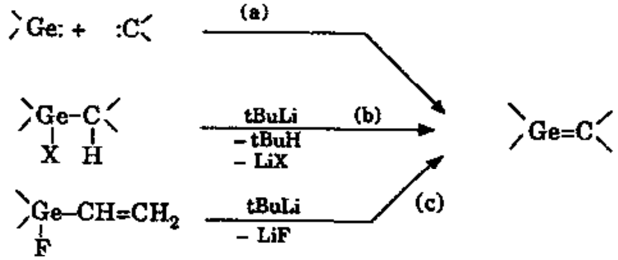
Among organogermanium compounds, many doubly bonded molecules have now been stabilized, such as germenes >Ge=C<, digermenes >Ge=Ge<, germaimines >Ge=N–, germaphosphenes >Ge=P– and germathiones >Ge=S. Some reviews have summarized this field [1–4]. This paper describes the synthesis, the physicochemical studies and the reactivity of such doubly bonded germanium species. Only those reactions involving stable compounds are described. Transient doubly bonded species, which have been reviewed recently [4], are not reported.

B. GERMENES, >Ge=C<

(i) Synthesis

Three routes allow the synthesis of stable compounds with a germanium–carbon double bond (eqn. (1)):

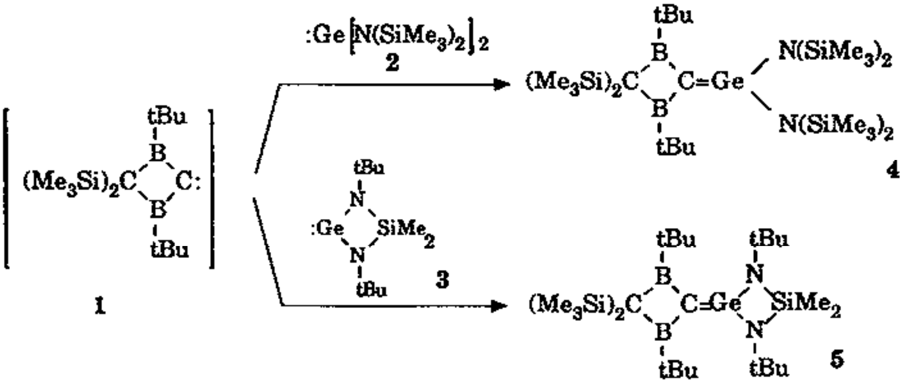
- coupling between a germylene and a carbene (route a)
- dehydrohalogenation of a halogermane by lithio compounds (route b)
- addition of an organolithio compound to a fluorovinylgermane followed by elimination of LiF (route c).



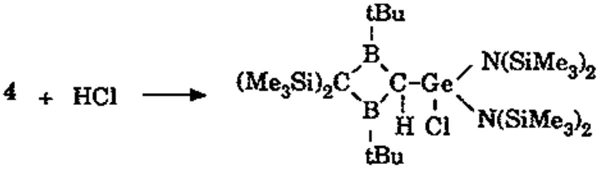
(1)

(a) Route a

The reaction, reported by Berndt et al., between the electrophilic cryptocarbene **1** [5] and the stable germylenes **2** [6] and **3** [7] afforded the stable germenes **4** and **5** [8] (eqn. (2)). Compounds **4** and **5** are stable at room temperature in solution. The presence of the Ge=C double bond in **4** has been confirmed by X-ray diffraction (see Section B(ii)(a)). Moreover, **4** has been chemically characterized by addition of HCl across the Ge=C double bond [8] (eqn. (3)).



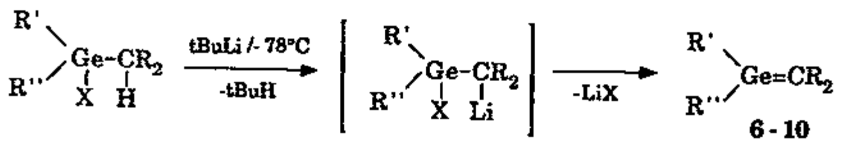
(2)



(3)

(b) Route b

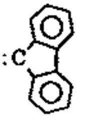
In our laboratory, five stable germenes **6–10** have been obtained by dehydrohalogenation of chloro- or fluorogermanes by tert-butyllithium [9-11] (eqn. (4)). Owing to the high germanium–fluorine bond energy (113 kcal/mol) [12], substitution of germanium by fluorine rules out the Li/halogen exchanges frequently observed when germanium is substituted by other halogens; therefore the best result is generally obtained with fluorogermanes, but the reaction must be done in some cases with chlorogermanes, particularly when the starting fluorogermanes are insoluble in Et_2O [10]. The use of a bulky lithio compound such as ${}^tBuLi$ is necessary to prevent direct alkylation of germanium. Addition of ${}^tBuLi$ to the halogermanes was performed at –78°C and under such conditions, the yields of germene are usually about 80%. Like **4** and **5**, germenes **6–10** are thermally stable but highly air- and moisture-sensitive derivatives obtained in the form of orange crystals.



(4)

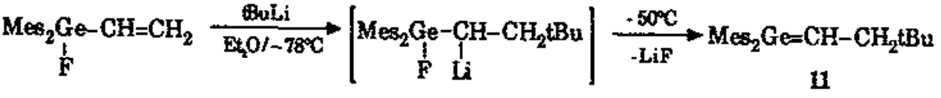
R'R'' : Mes$_2$ **6** [9] ; (R$_2$CH)$_2$ **7** [10] ; [(Me$_3$Si)$_2$CH]$_2$ **8** [11] ; Mes, (Me$_3$Si)$_2$CH **9** [11]; X:F

R'R'' : tBu, CHR$_2$ **10** [10] ; X : Cl ; CR$_2$:



(c) Route c

This route was described for the first time by Jones [13], and then widely used by Auner for organosilicon compounds [14] to obtain transient silenes from vinylchlorosilanes. By using bulky mesityl groups on germanium, the stable dimesitylneopentylgermene could be obtained in 90% yield [15] (eqn. (5)). Compound **11**, like the other germenes **6–10**, must be handled in an inert atmosphere and appears thermally stable.



(5)

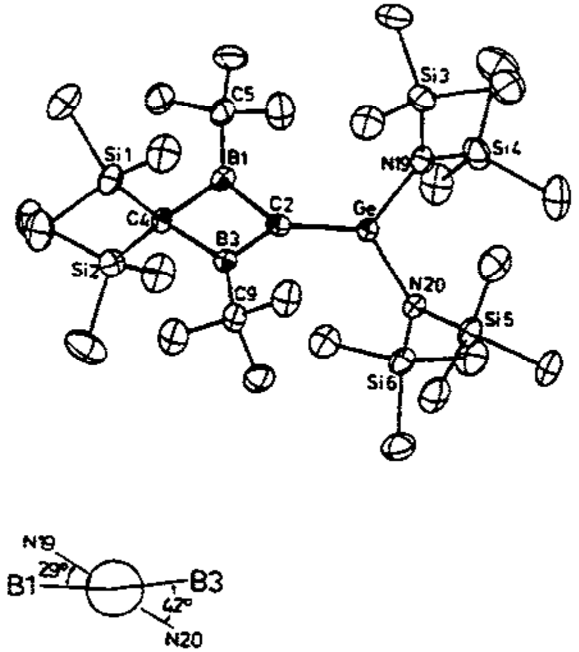
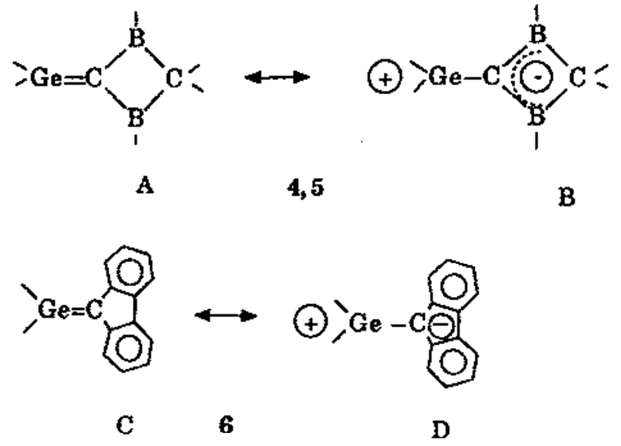


Fig 1. ORTEP view of **4** (reprinted from Angew. Chem. Int. Ed. Engl., 12 (1987) 221).

(ii) Physicochemical studies

(a) X-Ray structure determinations

X-Ray diffraction studies of **4** and **6** show short Ge–C distances (1.827 [8] and 1.801–1.806 Å [16], respectively), about 9–10% shorter than Ge–C single bonds, which are generally about 1.95–2.00 Å, depending on the degree of steric hindrance. Such shortening is typical of all doubly bonded main group elements [3,4,17–19]. The structure of **4** (Fig. 1) confirms the significance of the ylide resonance form B (eqn. (6)) as shown by short distances C(Ge)–B and an average twist angle at the Ge=C double bond of 36° [8].



(6)

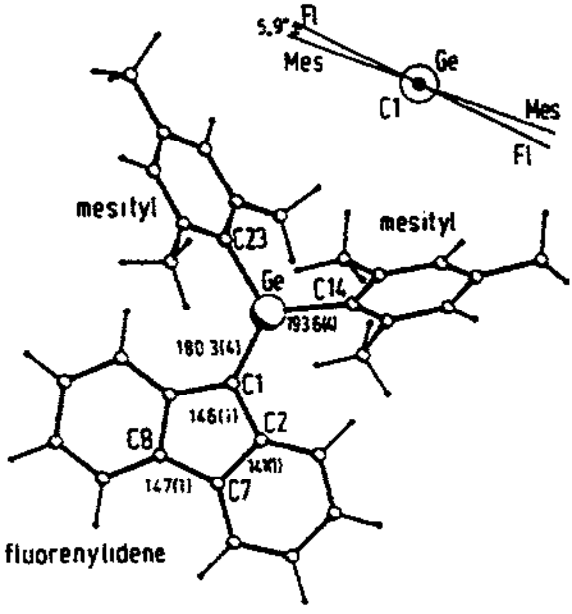


Fig 2. ORTEP view of **6** (reprinted from Angew. Chem. Int. Ed. Engl., 27 (1988) 828).

In **6**, a ylide form D could also be postulated since the negative charge on carbon can be delocalized on the fluorenylidene group (eqn. (6)). However, the X-ray structure of **6** [16] (Fig. 2) displays a planar germanium atom and a small twisting around the Ge–C bond (only 6°) consistent with structure C.

(b) Theoretical studies

The germanium–carbon double bond length (1.801–1.827 Å) is in good agreement with the sum of covalent radii (1.12 + 0.67 = 1.79 Å), with ab initio calculations using pseudopotentials (1.779 Å at the SCF level, 1.812 Å with configuration interactions) [20], and with other calculations (1.767, 1.782 [22c]; 1.761, 1.784, 1.814 [22d]). Calculations have also predicted a rather important polarity of the Ge–C double bond [20] (eqn. (7)), but less important than in silenes, which is in complete agreement with the chemical behavior of Ge=C bonds.

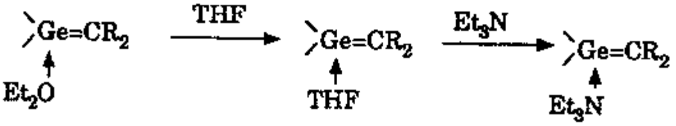
(7)

The π-bond energies of Group 14 metal–carbon double bonds have been determined by various methods. The results show that π-bond energies of silenes (35–36 kcal/mol [21]) and germenes (31 kcal/mol [21] or 32.2–33 [22d]) are similar, greater than for stannenes (19 [21] or 20.9, 21 kcal/mol [22d]), and smaller by about 30 kcal/mol than for alkenes (64–68 kcal/mol [21]). Thus these results show that the order of ability to form π-bonds is $C > Si \sim Ge > Sn$.

Ab initio calculations showed that germanium is more reluctant to form doubly bonded compounds than silicon [22a]. For example, although much more stable than germylmethylene $H_3Ge–CH$ [22b], the corresponding germene was predicted to be 11.4 [22c], 15 [20] and 24.2 kcal/mol [22a] less stable than methylgermylene $H_3C–GeH$; however, the energy barrier for the isomerization was calculated to be about 36 [22b] or 33.1 kcal/mol [22c]. The dipole moment of **6** is estimated to be 4 Debyes [16] indicating that the Ge=C double bond is strongly polar. The great importance of the resonance structure $Ge^+{=}C^-R_2$ explains its high stabilization due to the delocalization of the excess negative charge into the fluorenylidene system.

(c) NMR and Raman spectra

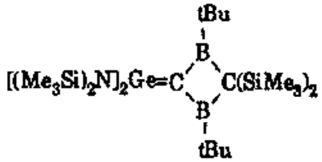
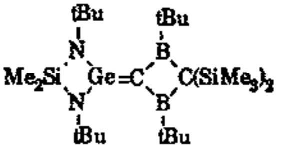
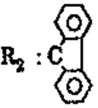
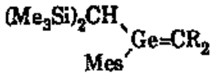
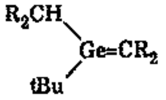
Germenes are very stable in the crystalline state and in non-polar solvents such as pentane or benzene. In polar solvents such as ethers or amines, **6**–**10** form Lewis acid-base adducts as shown by ^{1}H NMR [9] (eqn. (8)). This type of complexation has already been observed with silenes >Si=C< [23a], silaimines >Si=N– [23b] and recently in germaimines (see Section D) in which the double bond is strongly polarized and the metal highly electrophilic, but never in symmetric molecules M=M (M = Si, Ge, Sn, P) [17–19] or in metallaphosphenes >M'=P– (M' = Si, Ge, Sn) (see Section E) in which Group 14 metal is bonded to phosphorus, a less electronegative atom than carbon or nitrogen.



$$\underset{\underset{Et_2O}{\uparrow}}{>Ge=CR_2} \xrightarrow{THF} \underset{\underset{THF}{\uparrow}}{>Ge=CR_2} \xrightarrow{Et_3N} \underset{\underset{Et_3N}{\uparrow}}{>Ge=CR_2} \qquad (8)$$

TABLE 1

Germenes

	Germenes	Synthetic route[a]	d(Ge=C) (Å)	^{13}C (ppm)	Ref.
4		a	1.827	115	8
5		a		93	8
6	$Mes_2Ge=CR_2$ (CR_2 : )	b	1.801[b] 1.806		9,16
7	$(R_2CH)_2Ge=CR_2$	b			10
8	$[(Me_3Si)_2CH]_2Ge=CR_2$	b			11
9		b			11
10		b		79.8	10
11	$Mes_2Ge=CH-CH_2{}^tBu$	c		124.2	15

[a] (a) Coupling reaction between a germylene and a carbene; (b) dehydrohalogenation of a halogermane; (c) addition of ^{t}BuLi on a vinylfluorogermane, then elimination of LiF.

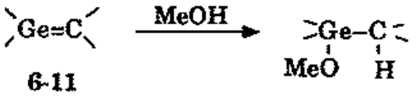
[b] Two crystallographic independent molecules.

Germenes have also been characterized by ^{13}C NMR which shows chemical shifts between 79.8 and 124.2 ppm [8,10,15] (see Table 1) for the sp^2 carbon doubly bonded to germanium. Unfortunately it is not possible to characterize sp^2 germanium by NMR as ^{73}Ge NMR is efficient only for symmetric tetracoordinated germanium species. The Raman spectrum of **6** shows a band at 988 cm^{-1} which is assigned to the Ge=C valence vibration [16], close to the calculated value of 1018 cm^{-1} using MNDO [16]. Other recent calculations predicted values of 785, 827 and 904 cm^{-1} [22d].

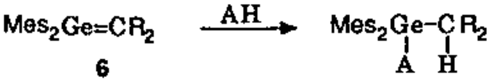
(iii) Reactivity

(a) Protic reagents. lithio compounds. disulfides. hydrides

Although bulky groups stabilize the Ge=C bond, **6–11** are extremely reactive towards various electrophiles and nucleophiles, and in cycloadditions. The most commonly used reagent to characterize germenes **6–11** is methanol which gives the corresponding methoxyadducts in nearly quantitative yield [9,10,11,15] (eqn. (9)). Other protic reagents react with germenes, for example HCl with **4** [8] and **11** [15], and thiols [9], hydrofluoric acid [9b] and imines, such as diphenylimine [24] with **6** (eqn. 10). Water gives two different products with **6** and **11**, depending on the quantity of water. With an excess, germanols **12** are obtained whereas with 0.5 equiv., digermoxanes **13** are formed, due to the reaction of germanol with unreacted germene [15,25] (eqn. 11).



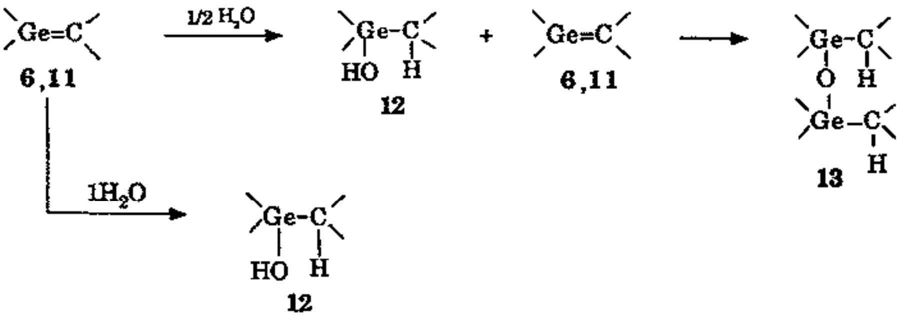
(9)



$$\underset{\mathbf{6}}{\mathrm{Mes_2Ge{=}CR_2}} \xrightarrow{AH} \mathrm{Mes_2}\underset{A}{\mathrm{Ge}}\mathrm{-}\underset{H}{\mathrm{C}}\mathrm{R_2}$$

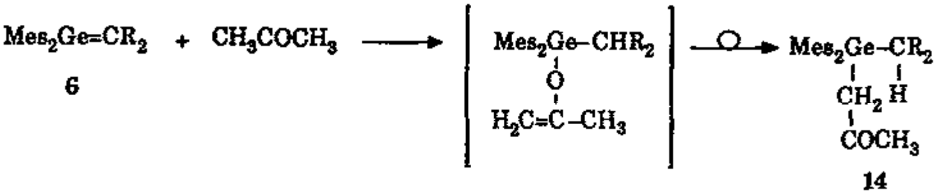
(10)

A: Cl, F, EtS, Ph$_2$C=N



(11)

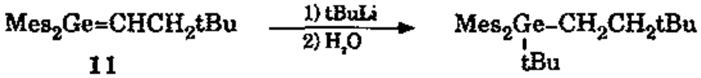
Enolyzable ketones such as acetone also react with **6** as protic reagents, yielding the derivative **14** [25] by a classic germanotropic rearrangement [26] (eqn. (12)). These reactions are regiospecific with the more negative group bonded to germanium.



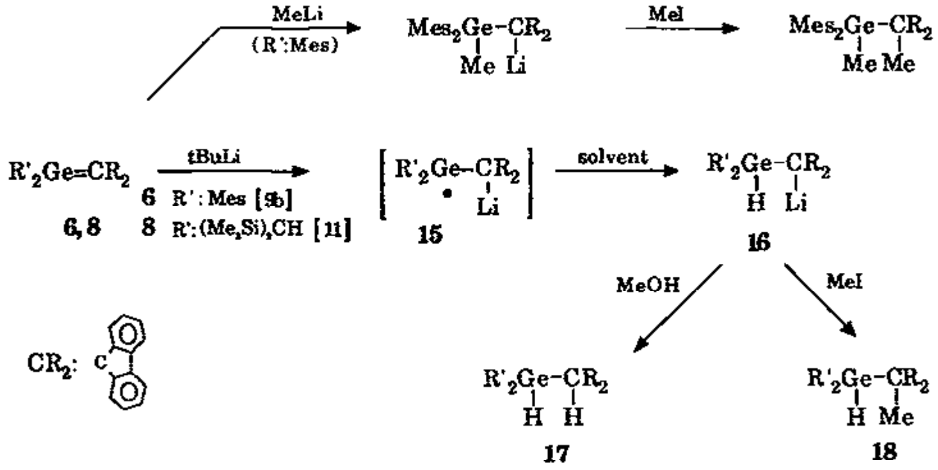
6 **14**

(12)

Lithio compounds give two types of reaction depending on steric hindrance. Methyllithium adds to the double bond of **6** to afford the corresponding germane [9b] after quenching with methyl iodide (eqn. (14)). The same type of addition to the Ge=C double bond is observed between tert-butyllithium and germene **11** [15] (eqn. (13)). A completely different reaction occurs between tert-butyllithium and germenes **6** and **8** which have a more pronounced steric hindrance around the double bond than **11**. After quenching with methanol or methyl iodide, the germanes **17** and **18**, respectively, are obtained. These reactions are best explained by a single-electron transfer mechanism involving the intermediates **15** and **16** (eqn. (14)).



$$\underset{\mathbf{11}}{Mes_2Ge{=}CHCH_2tBu} \xrightarrow[2)\,H_2O]{1)\,tBuLi} \underset{tBu}{Mes_2\underset{|}{Ge}{-}CH_2CH_2tBu} \qquad (13)$$

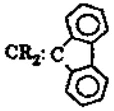


6,8 **15** **16** **17** **18**

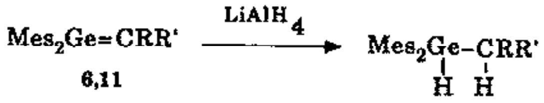
(14)

Disulfides such as dimethyldisulfide also add to the germanium–carbon double bond, probably according to a radical mechanism [9] (eqn. (15)). The double bond of **6** and **11** can be easily reduced by lithium aluminium hydride (eqn. (16)).

$$\underset{\mathbf{6}}{Mes_2Ge{=}CR_2} \xrightarrow{MeSSMe} Mes_2\underset{MeS}{Ge}{-}\underset{SMe}{CR_2}$$

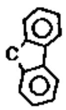


(15)



$$\underset{\mathbf{6,11}}{Mes_2Ge{=}CRR'} \xrightarrow{LiAlH_4} Mes_2\underset{H}{Ge}{-}\underset{H}{C}RR'$$

(16)

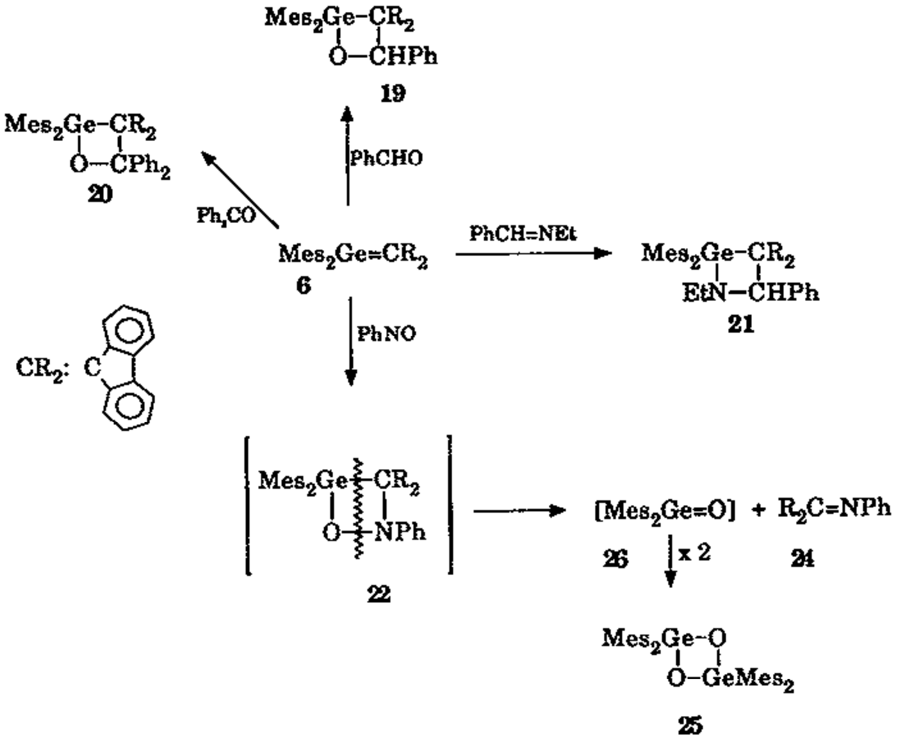
CRR':  **6** [9]; $CHCH_2tBu$ **11** [15]

(b) [2+2] Cycloadditions: aldehydes and ketones, imines, nitroso compounds

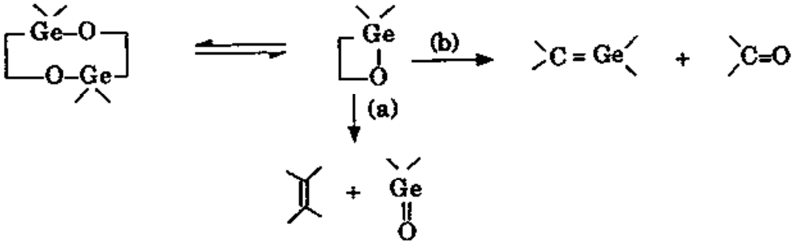
Germenes, and particularly germene **6** which has been the most intensively studied, are very reactive in cycloadditions. Nearly quantitative [2+2] cycloadditions are observed with aldehydes [25], ketones [25], nitrosobenzene [24] at ambient temperature, and imines [24] after heating at 140°C in a sealed tube (eqn. (17)). Four-membered ring derivatives **19** and **20** are thermally very stable contrary to other heterocycles of this type which generally dimerize [27] or decompose by a [4] → [2+2] process, with formation of germanone and alkene (route a), or by cycloreversion (route b) to give the starting material (eqn. (18)).

The process (b) has been observed by Wiberg in the four-membered ring compounds obtained by addition of benzophenone to the transient germene $Me_2Ge{=}C(SiMe_3)_2$ [28]. Thus, this germaoxetane is a convenient storage device for this germene. Heterocycles **19** and **20** are stable to oxidation and hydrolysis, even towards acetic acid. The chemical inertness of the Ge–O bond in these heterocycles is probably due to the large steric hindrance caused by mesityl groups on germanium, as clearly demonstrated by the X-ray structure.

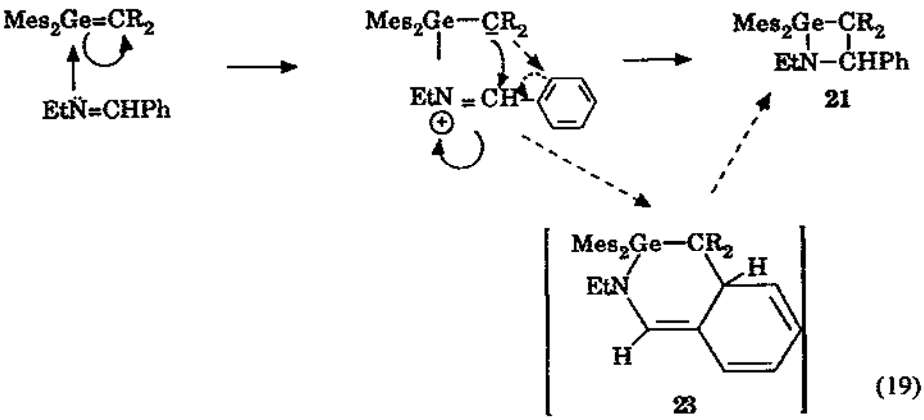
Reaction of **6** with nitrosobenzene affords only the imine **24** and the 2,4-digerma-1,3-dioxetane **25**, a dimer of the transient germanone **26** [24]. These products probably involve the preliminary formation of the four-membered ring heterocycle **22** followed by a classical [4] → [2+2] decomposition. Imines are much less reactive than carbonyl compounds towards germene **6** and a prolonged heating at 140°C in a sealed tube is necessary for the reaction [24]. As in the case of benzaldehyde and benzophenone, a [2+4] cycloaddition has never been observed although the preliminary formation of the six-membered heterocycle **23**, followed by its isomerization to **21** is not excluded (eqn. (19))


Mes₂Ge–CR₂
O–CHPh
19
Mes₂Ge–CR₂
O–CPh₂
20
PhCHO
Ph₂CO
Mes₂Ge=CR₂
6
PhCH=NEt
Mes₂Ge–CR₂
EtN–CHPh
21
PhNO
CR₂: C
Mes₂Ge–CR₂
O–NPh
22
[Mes₂Ge=O] + R₂C=NPh
26
x 2
24
Mes₂Ge–O
O–GeMes₂
25

(17)


Ge–O
O–Ge
Ge
O
(b)
C = Ge
+
C=O
(a)
+
Ge
O

(18)

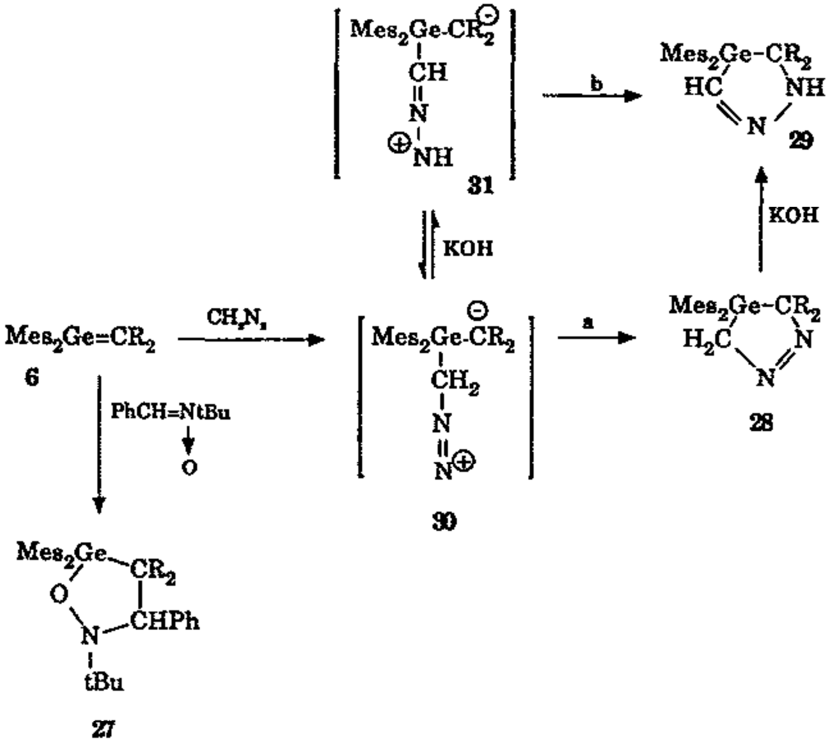

Mes₂Ge=CR₂
EtN=CHPh
Mes₂Ge—CR₂
EtN = CH
Mes₂Ge–CR₂
EtN–CHPh
21
Mes₂Ge—CR₂
H
EtN
H
23

(19)

(isomerization of a six-membered ring to a four-membered ring has been postulated by Wiberg in the formation of silaoxetanes from silenes and ketones [29]).

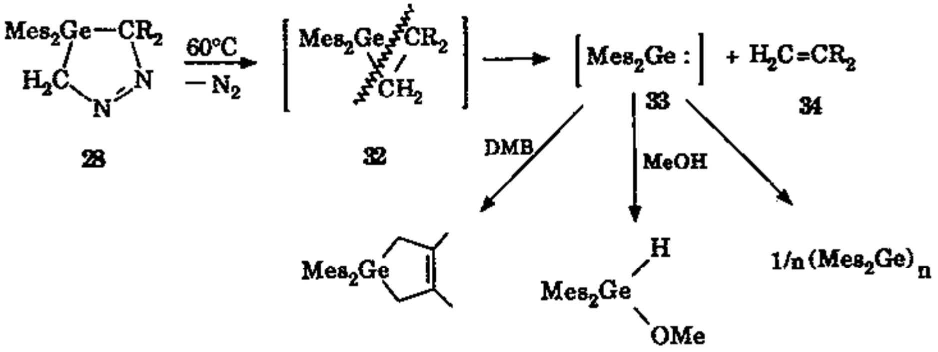
(c) [2+3] Cycloadditions: nitrones and diazo compounds

Facile [2+3] cycloadditions have been observed between **6** and *N*-(tert-butyl)-α-phenylnitrone and diazomethane leading to the five-membered heterocycles **27** [9a], **28** [30,31] and **29** [30] (eqn. (20)). The reaction with diazomethane is very dependent on experimental conditions. When a large excess of an ethereal solution of diazomethane, dried over potassium pellets, was added to a solution of **6** in Et_2O at –78°C, the only observable product was the germapyrazoline **29** [30]. When the reaction was carried out with a solution of distilled diazomethane (thus free of traces of KOH), the 4-germa-1-pyrazoline **28** was obtained [30,31]. The first steps of these reactions are probably the formation of the dipolar intermediates **30** or **31**. Such a prototropy leading to **29** from **28** is well known and has already been observed in other five-membered rings containing the CH_2–N=N linkage [32]. The reverse addition of diazomethane to the Ge=C double bond, with nitrogen bonded to germanium, has never been observed.



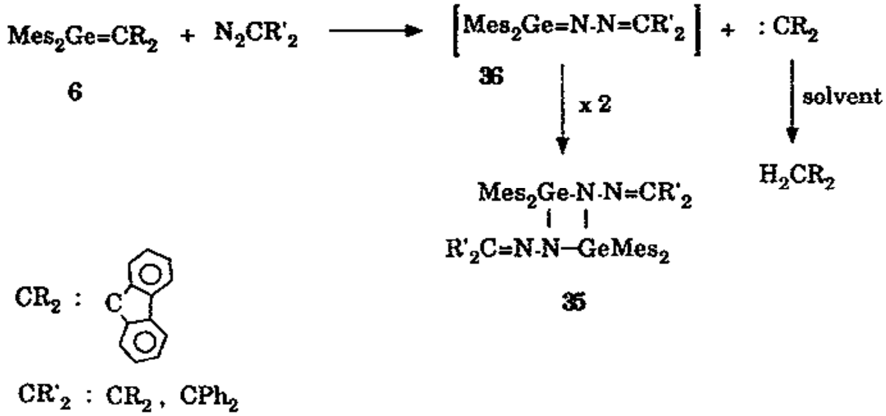
(20)

Compound **28** was of particular interest as a potential precursor of three-membered ring germiranes **32** (eqn. (21)) which are still unknown, contrary to stable siliranes [33]. Heating **28** at 60°C does not afford the germirane **32**, but only 9-methylenefluorene **34**, and oligomers $(Mes_2Ge)_n$ according to a decomposition [3] → [2+1] already observed with siliranes. The transient germylene has been trapped by methanol [30] or dimethylbutadiene [31]. Attempts to trap germirane have been unsuccessful probably because of its very short lifetime.



(21)

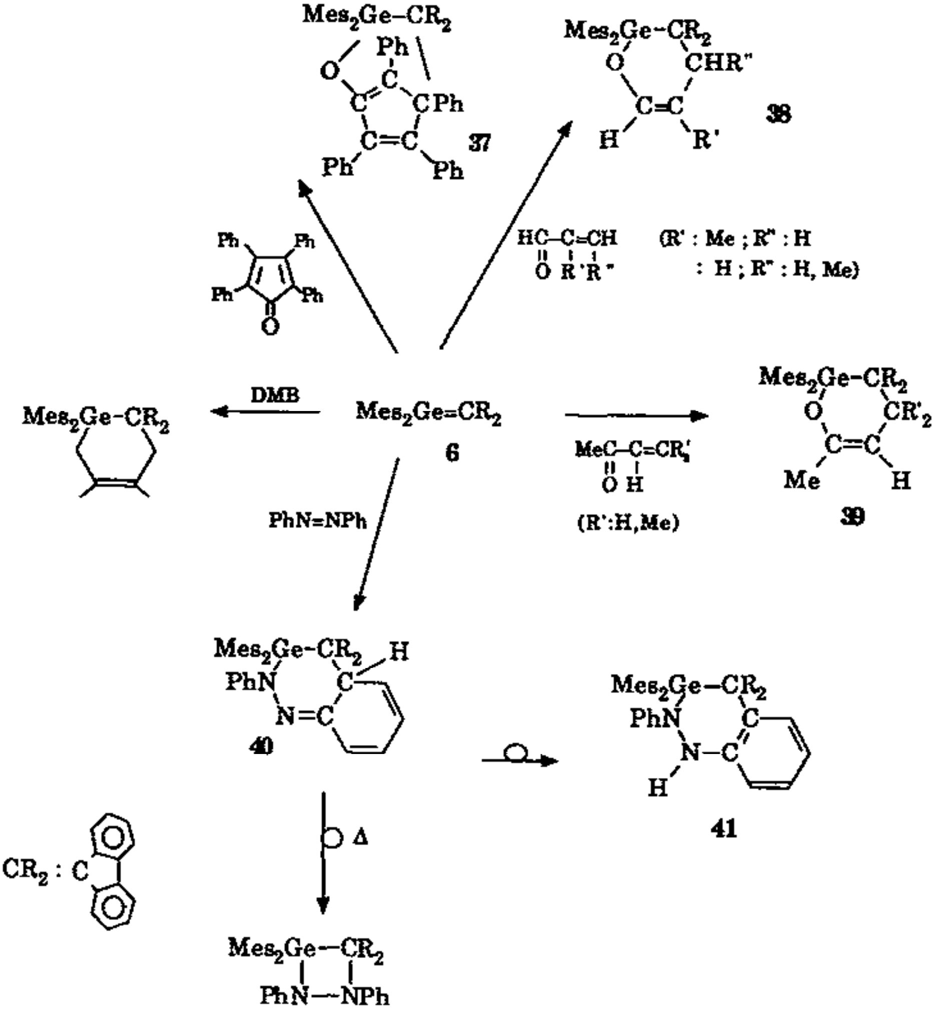
Other diazo compounds such as diazofluorene or diphenyldiazomethane give a completely different reaction with **6**, leading to the digermadiazetidines **35** and fluorene R_2CH_2 exclusively [34]. A mechanistic study seems to prove the formation of germaimine **36** as an intermediate, followed by its dimerization (eqn. (22)). In the case of diazofluorene, the dimerization of germaimine **36** affords only the cyclodigermazane **35** with the R'_2CN in a *cis* position, which then quantitatively isomerizes to the *trans* isomer (as characterized by X-ray) after a week at room temperature in solution.



(22)

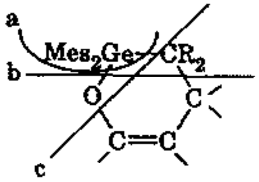
(d) [2+4] Cycloadditions: dienes, azobenzene, α-ethylenic aldehydes and ketones

[2+4] Cycloadditions have been observed between germene **6** and 2,3-dimethylbutadiene [9a], azobenzene [24] and various α-ethylenic aldehydes and ketones [35] (eqn. (23)). With 2,3-dimethylbutadiene, only the [2+4] cycloaddition occurs, whereas an enereaction or a [2+2] cycloaddition with the C=C double bond have not been observed [9a].



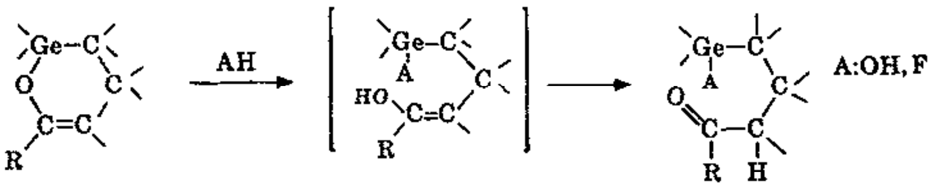
(23)

Although the α-ethylenic aldehydes and ketones have different steric and electronic properties, as well as different charges on carbons 2 and 4 [36], exclusive [2+4] cycloaddition leading to the corresponding six-membered ring germaoxacyclohexenes 37–39 [35] have been observed. In the mass spectrum, the most important fragment is always (except for 37) the germylene Mes_2Ge^+. This can arise from the germene $[Mes_2Ge{=}CR_2]^+$ as observed in most cases (fragmentation b), but more likely, from a [6] → [5+1] decomposition, since the $R_2C–C–C=CO$ moieties are also observed (fragmentation a). So it seems that the two types of fragmentation, a and b, occur in germaoxacyclohexenes **38**, **39**, whereas path c appears as a minor one since $[Mes_2Ge=O]^+$ is observed less frequently (eqn. (24)).



(24)

The structure of these adducts is supported by their physicochemical data and also by their chemical reactivity. Addition of water or HF to **38** and **39** gives aldehydes and ketones, respectively, after cleavage of the Ge–O bond (eqn. (25)).

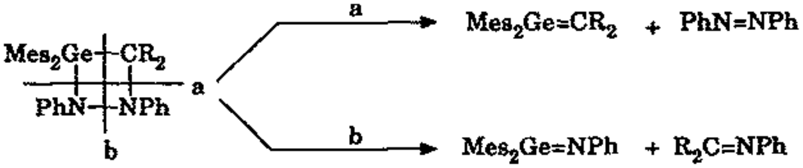


38,**39**

(R: H, Me)

(25)

Azobenzene gives only a [2+4] cycloaddition involving one of the phenyl groups; the reaction occurs at room temperature with formation of **40** [24] (eqn. (23)). After a few days in solution, compound **41** was formed, the driving force of the rearrangement **40** → **41** being the re-aromatization. On the contrary, heating **40** leads to the four-membered ring **42**. Thermolysis of **42** gives the two expected types of fragmentation [4] → [2+2], with formation of starting material (a), of germaimine **43** and the corresponding imine (b) (eqn. (26)).



43

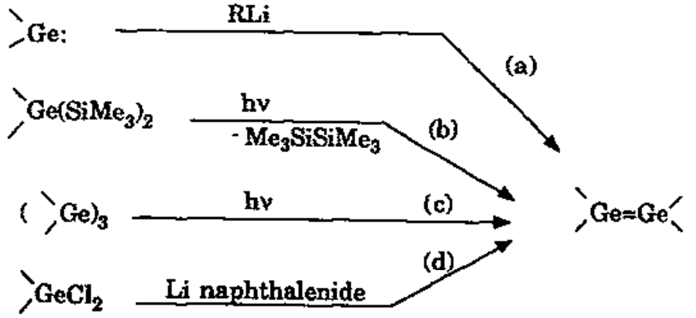
(26)

C. DIGERMENES >Ge=Ge<

(i) Synthesis

Stable digermenes are obtained by four routes (eqn. (27)):

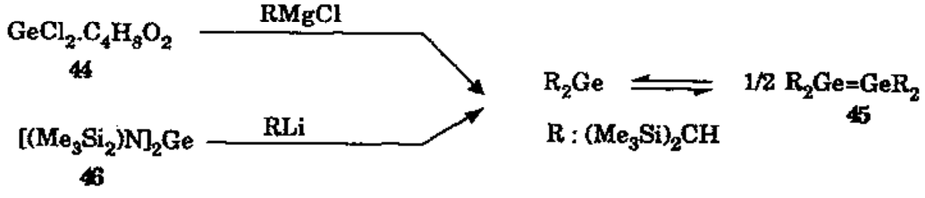
- reaction of aryl- or alkyllithio compounds with a stable germylene (route a);
- coupling of germylenes obtained by irradiation of bis-silylgermanes (route b);
- irradiation of cyclotrigermanes (route c);
- reaction of diaryldichlorogermanes with lithium naphthalenide (route d).



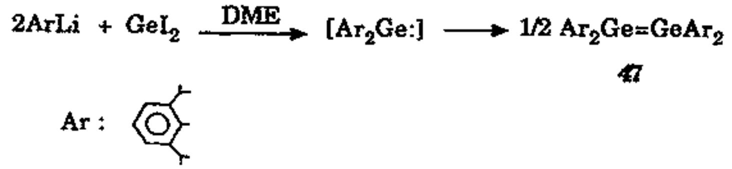
(27)

(a) Route a

Route (a) was used by Lappert to prepare digermene **45** [37], using bisyllithium, $(Me_3Si)_2CHLi$, with stable germylene **46** or a Grignard reagent with dichlorogermylene–dioxane complex **44**. These reactions afforded **45** in good yield (eqn. (28)). Compound **45** was the first digermene to be prepared, but it retains its digermene structure only in the solid state, and in solution it behaves as two germylene species (see below). Digermene **47** [38] can also be synthesized in low yield (10%) by reaction of diiodogermylene, GeI_2, with 2 equiv. of 2,6-diisopropylphenyllithium, resulting in the formation of the transient germylene, Ar_2Ge, followed by its dimerization (eqn. (29)).



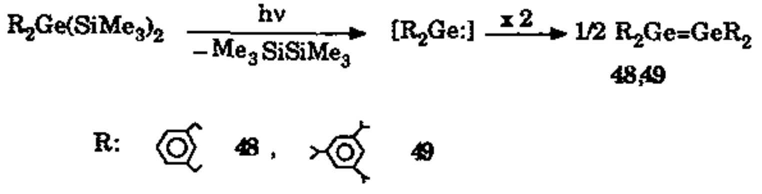
(28)



(29)

(b) Route b

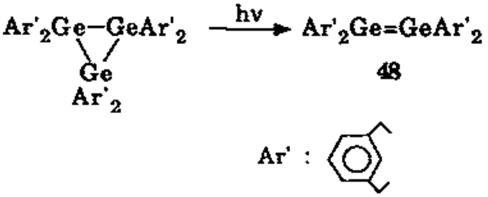
Irradiation of bis(trimethylsilyl)germanes gives the corresponding germylenes which dimerize to digermenes [3,39–41]. This route allowed the synthesis of **48** [39], which was the first digermene to retain its Ge=Ge structure in solution, and of **49** [42a] (eqn. (30)). This route also affords other transient digermenes which dimerize at room temperature because they are substituted by less bulky groups such as two 2,6-dimethylphenyl, two mesityl, a mesityl and a tert-butyl, a mesityl and a 2,6-diethylphenyl [3]. In the organosilicon field, the dimerization of a silylene obtained by photolysis of an acyclic trisilane was the first route to tetramesityldisilene [43].



$$R_2Ge(SiMe_3)_2 \xrightarrow[-Me_3SiSiMe_3]{h\nu} [R_2Ge:] \xrightarrow{\times 2} 1/2\ R_2Ge{=}GeR_2 \quad \textbf{48,49} \tag{30}$$

(c) Route c

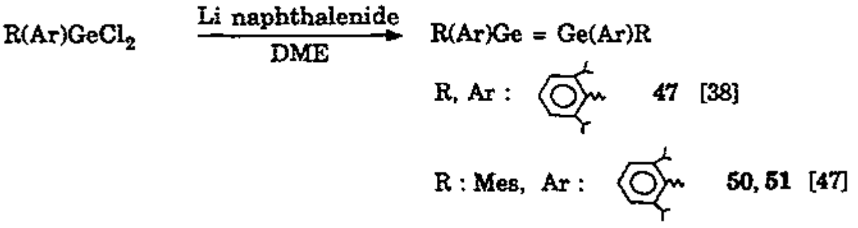
The photolysis of a cyclotrigermane was the first access to a transient digermene substituted by the 2,6-dimethylphenyl group [44]. However, this digermene could not be isolated because of its slow conversion to the starting cyclotrigermane. Other digermenes have been obtained by this route [3]. The only clean reaction is observed in the case of **48** (eqn. (31)) [45] from the corresponding cyclotrigermane [42b,45]. A similar route involving the irradiation of cyclotrisilanes or of a cyclotristannane was employed for the synthesis of disilenes [18] and a distannene [46].



$$\xrightarrow{h\nu} Ar'_2Ge{=}GeAr'_2 \quad \textbf{48} \tag{31}$$

(d) Route d

The treatment of diaryldichlorogermanes with lithium naphthalenide afforded the corresponding digermenes [38,47] (eqn. (32)). This route is particularly useful for the synthesis of digermenes bearing very large substituents, which cannot be obtained by route (c) since the synthesis of cyclotrigermanes is impossible due to the excessive steric hindrance.



$$R(Ar)GeCl_2 \xrightarrow[DME]{\text{Li naphthalenide}} R(Ar)Ge = Ge(Ar)R \tag{32}$$

(ii) Physicochemical studies

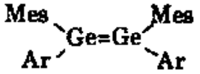
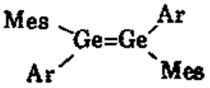
(a) X-Ray diffraction

The X-ray crystal structure has been determined for digermenes **45**, **48** and **50**. The Ge=Ge bond length is very different in the three derivatives: 2.213 Å in **48** [45,47], 2.30 Å in **50** [47] and 2.347 Å in **45** [48,51] (sum of covalent radii 2.24 Å) (see Table 2). These long bonds are probably due to an increase in the size of substituents. Lappert's digermene **45** (see Fig. 3), which has the longest Ge–Ge distance, retains its structural integrity only in the crystal [48] and reacts as two germylenes in solution. There is a rather good agreement with calculations which predicted bond lengths of 2.27–2.341 Å depending on the method used [22c,d,49b].

Digermenes **45** and **50** have a markedly *trans* conformation with a fold angle of 32 and 36°, respectively (eqn. (33)). Such fold angles correspond to calculations which predict values from 34 to 40° (depending on the basis set used) [3,48,49]. On the contrary, **48** (see Fig. 4), which contains two smaller groups on germanium than **45** and **50**, is more planar, with a fold angle of only 12°. The structure of germene **45** has been described according to eqn. (33) [48].

TABLE 2

Digermenes

	Digermenes	Synthetic route[a]	UV nm (log ε)	Fold angle (°)	d(Ge=Ge) (Å)	Ref.
45	$R_2Ge{=}GeR_2$ $(R = (Me_3Si)_2CH)$	a	302 (3.2) 414 (3.0)	32	2.35	37 48
47	$Ar_2Ge{=}GeAr_2$ Ar = 	a,d	418 (4.6)	–	–	38
48	$Ar'_2Ge{=}GeAr'_2$ Ar' = 	b,c	412 (3.9)	12	2.21	39 45 47
49	$Ar''_2Ge{=}GeAr''_2$ Ar'' = 	b	305 (4.0) 418 (4.5)	–	–	42
50	 $(Mes)(Ar)Ge{=}Ge(Mes)(Ar)$	c,d	–	36	2.30	47
51	 $(Mes)(Ar)Ge{=}Ge(Ar)(Mes)$	c,d	412 (4.6)	–	–	47

[a] (a) Reaction of lithio compound with a stable germylene; (b) coupling of germylenes obtained by irradiation of bis-silylgermanes; (c) irradiation of cyclotrigermanes; (d) reaction of dichlorogermanes with lithium naphthalenide.

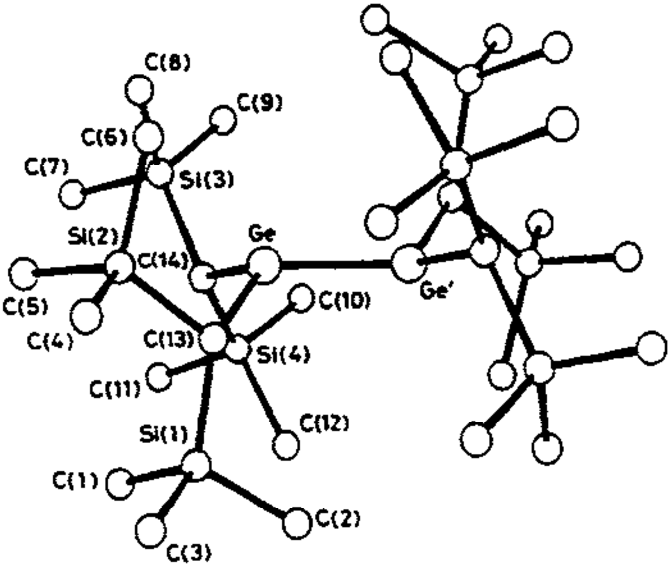


Fig. 3. Molecular structure of **45** (reprinted from J. Chem. Soc. Chem. Commun.,.(1984) 480).

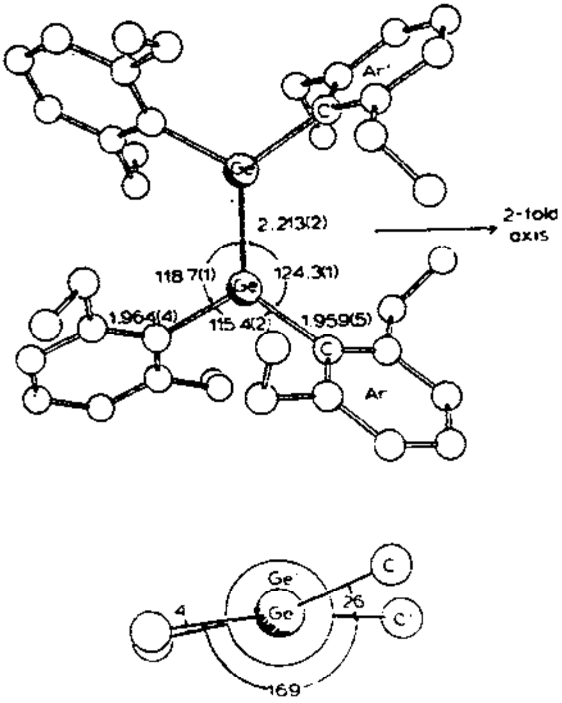
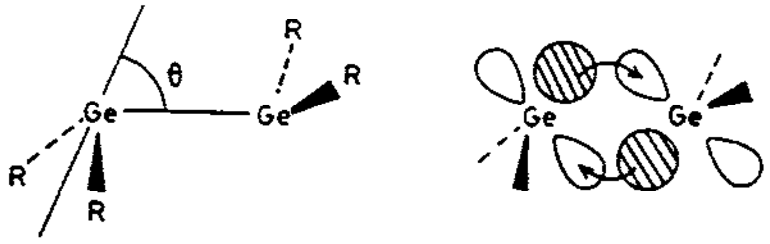


Fig. 4. Molecular structure of **48** (reprinted from Tetrahedron Lett., 25 (1984) 4191).

Note that the fold angles in digermenes are much greater than in disilenes which are generally more planar and, in some cases, completely planar with fold angles and twist angles of 0° [3]. The twist angles in digermenes **45**, **47** and **51** are small, 0, 10 and 7°, respectively.



(33)

(b) UV spectra

Like other doubly bonded main group species, digermenes are usually yellow. The absorptions of digermenes are blue-shifted compared to those of disilenes but considerably red-shifted from those of ethenes and are not affected by their conformation. The longest wavelength absorptions (between 412 and 418 nm) (see Table 2) have been attributed to a transition between modified π and π^* orbitals [3].

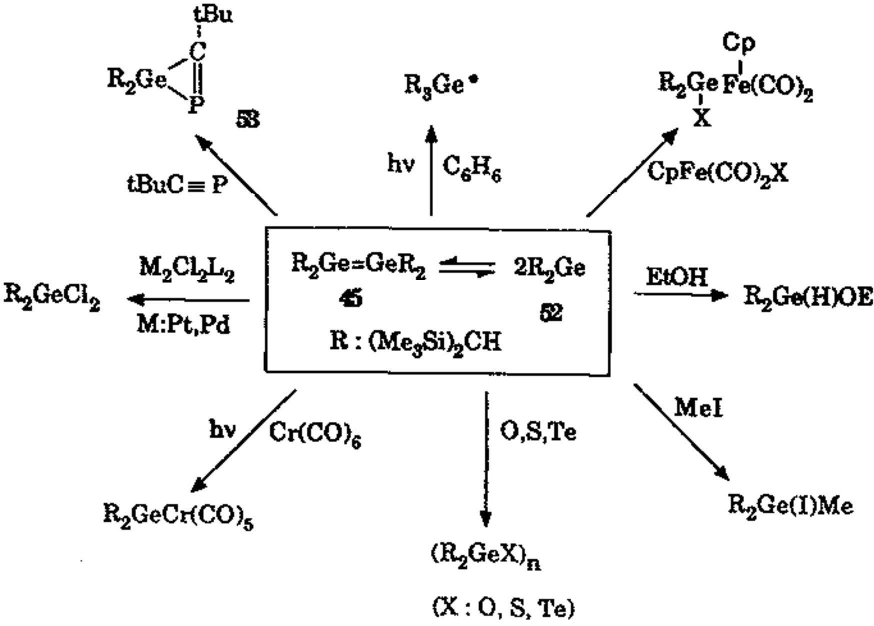
(c) Energy of the Ge=Ge double bond

The synthesis of *Z* or *E* stereoisomers **50** and **51** [47] provides a means to determine the activation energy of the isomerization, which is 20.0 ± 0.3 kcal/mol for $E \rightarrow Z$ (**50** → **51**) and 22.2 ± 0.3 kcal/mol for $Z \rightarrow E$ (**51** → **50**) [47]. These values are in good agreement with calculations of the enthalpy of activation for the Ge=Ge bond isomerization, which are estimated at 25 [49e] and 25.4–28 [22d] kcal/mol. In disilenes, the values are about 4–7 kcal/mol higher [3]. The dissociation energy of **48** was estimated, by kinetic investigation, at an upper limit of 30 kcal/mol [3]. Calculations predict this dissociation energy to be between 30 and 45 kcal/mol for digermenes [48,49b,50].

(iii) Reactivity

Like all the doubly bonded main group species, the digermenes are extremely air- and moisture-sensitive, but they can be stored for long periods in an argon or a nitrogen atmosphere. Although a large steric hindrance is necessary for their stabilization, they appear very reactive, showing double bond characteristics toward certain reagents. As noted previously, **45** retains its digermene structure only in the solid state. The reactivity of **45** involves the corresponding germylene **52** (eqn. (34)). Most of the reactions lead to tetravalent germanium compounds (e.g. with MeI, EtOH, $M_2Cl_2L_2$ (M = Pt, Pd), O, S, Te) [48]. Transition metal complexed germylenes are also obtained from **45** as well as germyl radicals $R_3Ge^{\cdot}$ by irradiation in benzene [51]. Recently, the first germaphosphirene **53** [52] was synthesized by reacting **45** $\rightleftharpoons$ **52** with tert-butylphosphaalkyne (eqn. (34)). A similar behavior occurs for the tin analogue of **45** which appears as a distannene

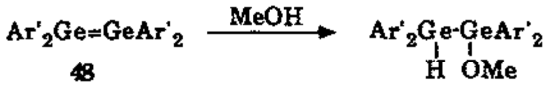
$R_2Sn{=}SnR_2$ in the solid state by X-ray diffraction and behaves as a stannylene R_2Sn in solution [54]. In sharp contrast, among silenes, the analogue of **45** retains its disilene structure $R_2Si{=}SiR_2$ ($R = (Me_3Si)_2CH$) in solution [55].



(34)

(a) Alcohols

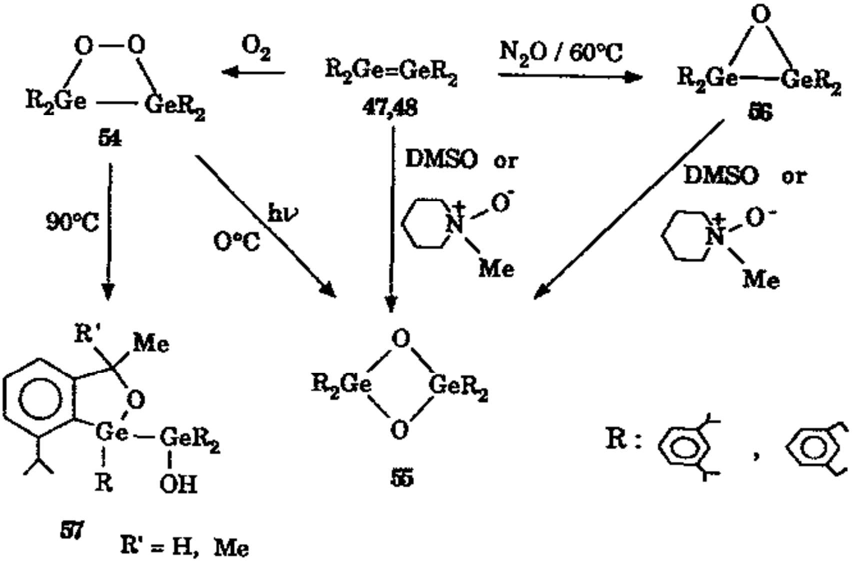
The great difference between digermene **45** and other digermenes appears in their chemical behavior; for example, **48** gives the corresponding methoxydigermane with methanol (eqn. (35)), whereas digermene **45** displays the reaction of germylene shown previously in eqn. (34). This reaction proves that digermene **48**, contrary to **45**, retains its structural integrity in solution.



$$\underset{\mathbf{48}}{Ar'_2Ge{=}GeAr'_2} \xrightarrow{MeOH} Ar'_2\underset{H}{Ge}{-}\underset{OMe}{Ge}Ar'_2 \qquad (35)$$

(b) Oxidation

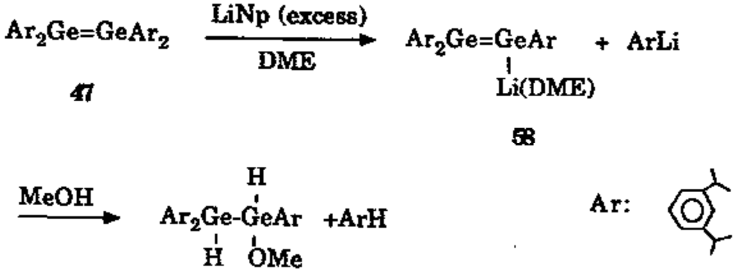
Digermenes **47** and **48** undergo oxygenation through various pathways [53] (eqn. (36)). Exposure of **47** or **48** to oxygen gives **54** quantitatively, which isomerizes to **57** on heating, whereas **54** gives **55** upon photolysis. This last derivative can also be obtained directly and quantitatively from digermenes by reaction with DMSO or *N*-methylmorpholine-*N*-oxide. The digermoxirane **56** also results from **47** or **48** by oxidation with N_2O at 60°C [53] (eqn. (36)).



(36)

(c) Reaction with lithium naphthalenide

Addition of an excess of lithium naphthalenide to **47** produces the unexpected cleavage of a Ge–Ar bond to give the corresponding digermenyllithium **58** [38], the first compound of this type in Group 14 metal chemistry (eqn. (37)). A different reaction is observed with less hindered digermene **48** since, in this case, cleavage of the germanium–aryl bond does not occur. Instead, digermane **59** (due to the reduction of the Ge–Ge double bond), Ar'_2GeH_2, and unidentified polymers were obtained [3] (eqn. (38)).



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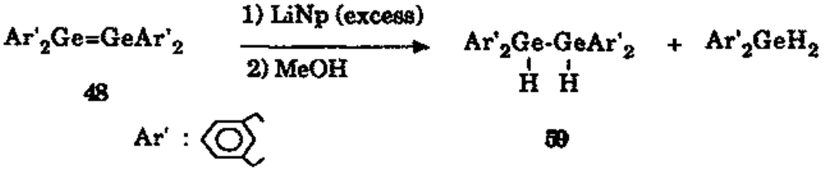


(38)

(d) [2+1] Cycloadditions

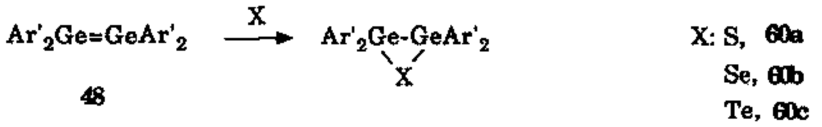
Digermene **48** reacts with S [56], Se [56] and Te [57] to give the corresponding air-stable thia-, selena- or telluradigermiranes in good yields (eqn. (39)). These heterocycles show temperature-dependent NMR spectra due to the slow rotation of the aryl groups caused by large steric hindrance [56]. Telluradigermirane exhibits thermochromism, being colorless at −196°C, pale yellow at room temperature, and orange at about 140°C [57]. The structures of **60a** and **60b** have been determined by X-ray crystallographic analyses [3], and show relatively short germanium–germanium bond distances (2.387 and 2.398 Å; cf. 2.44 Å in a standard Ge–Ge bond) and nearly planar arrangements of the two germanium atoms and of the four ipso carbon atoms of the aryl groups (the sum of angles on germanium is 357.3 and 356.7°). As short Ge–Ge bond distances are not characteristic of three-membered rings (cyclotrigermanes have a longer Ge–Ge bond than expected [44] [59]), these results can be interpreted in terms of Dewar's model of metal olefin bonding [60,61]. Thus, **60a** and **60b** should have some π-complex character (form A) (eqn. (40)). Similar structures have been reported in other three-membered heterocycles:

Ge–Ge–X (X = CH_2, NPh; see Section C(iii)(f)

Si–Si–X (X = O,S, CH_2, $NSiMe_3$)

Ge–S–P (see Section E)

In compound **60c** [57], the X-ray structure also shows that the ipso carbons of the aryl groups and the germanium atoms are almost coplanar (sum of angles on germanium 355.4 and 355.5°). But in contrast to **60a** and **60b**, the normal Ge–Ge bond length (2.435 Å) does not support the π-complex model. Similar [2+1] cycloadditions with sulfur and selenium have also been obtained from the metastable tetramesityldigermene $Mes_2Ge{=}GeMes_2$ [57,58].



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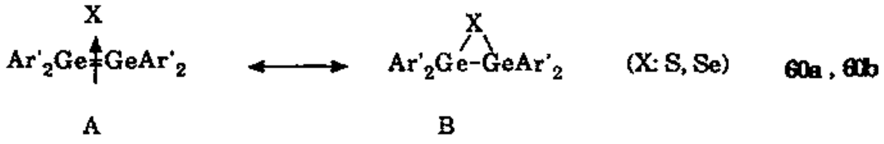
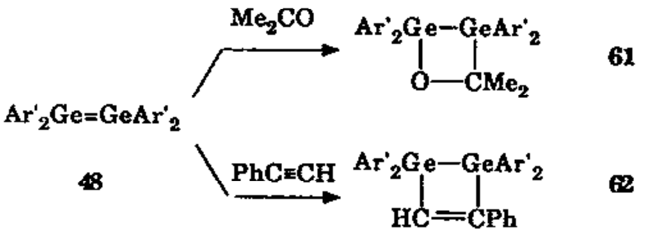


(40)

(e) [2+2] Cycloadditions

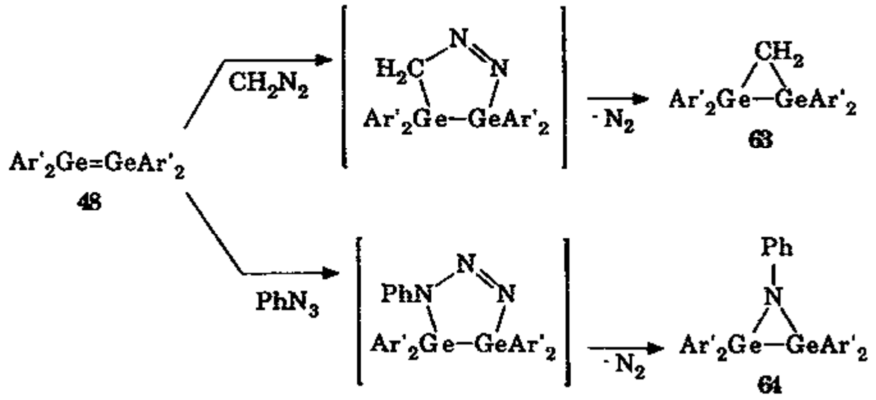
Acetone and diphenylacetylene undergo [2+2] cycloadditions with digermene **48** to give the corresponding four-membered ring derivatives **61** and **62** [56] (eqn. (41)). In sharp contrast, acetone and acetophenone react only as protic reagents with germenes >Ge=C< and germaphosphenes >Ge=P–, which have polar bonds (see Sections (B(iii) and E(iii)).



(41)

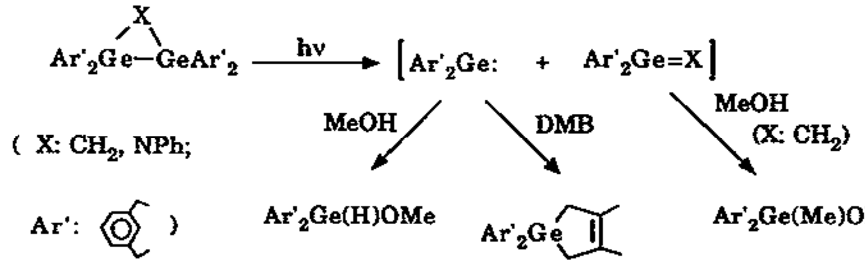
(f) [2+3] Cycloadditions

Digermene **48** undergoes [2+3] cycloadditions in good yields with diazomethane and phenylazide [42a,56] (eqn. (42)). As for compounds **60a** and **60b** [3], short Ge–Ge distances and planarity around the germanium atoms are observed for **63** and **64** [42a], hence a π-complex can also be postulated for these cycloadducts.



(42)

Photolysis of the two three-membered ring compounds **63** and **64** shows them to be good precursors of germylene Ar'$_2$Ge (which have been trapped by DMB and methanol) and of the corresponding germene and germaimine [42a] (eqn. (43)). However, only the germene could be confirmed by trapping with methanol. The germaimine probably polymerizes rapidly [42a] (eqn. (43)).



(43)

Interestingly [2+4] cycloadditions from stable digermenes (for example with dienes or α-ethylenic aldehydes and ketones) have never been observed. Diels–Alder reactions with dienes have only been obtained from transient digermenes such as $Et_2Ge=GeEt_2$ [62]. Other types of cycloadditions have also been observed with transient digermenes (see [4] and refs. therein).

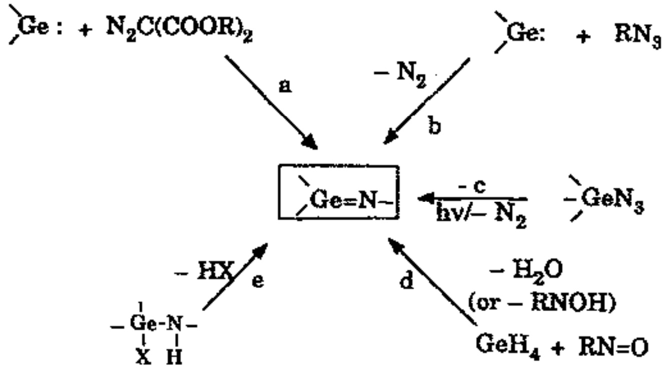
Until now, no stable germasilenes $R_2Ge=SiR_2$ or stannagermenes $R_2Sn=GeR_2$ have been synthesized. However, very recently, the transient germasilene $Mes_2Ge=SiMes_2$ has been obtained by Baines et al. by photolysis of hexamesityldigermasilirane and characterized by a trapping reaction with methanol and ^{29}Si NMR at –70°C [122]. At room temperature, this germasilene isomerizes to the corresponding silylgermylene $Mes_3Si–GeMes$ [122], in accordance with calculations which predicted that silylgermylene is more stable than germasilene by 3–6 kcal/mol [50,122].

D. GERMAIMINES $>Ge=N-$

(i) Synthesis

Stable germaimines are obtained by five routes (eqn. (44)):

- coupling of germylenes with diazomalonic esters (route a);
- coupling of germylenes with azides (route b);
- photolysis of a germylazide (route c);
- reaction between germane and nitroso or nitroxy compounds (route d);
- dehydrochlorination (or fluorination) of a chloro- (or fluoro)germylamine by tert-butyllithium (route e).



(44)

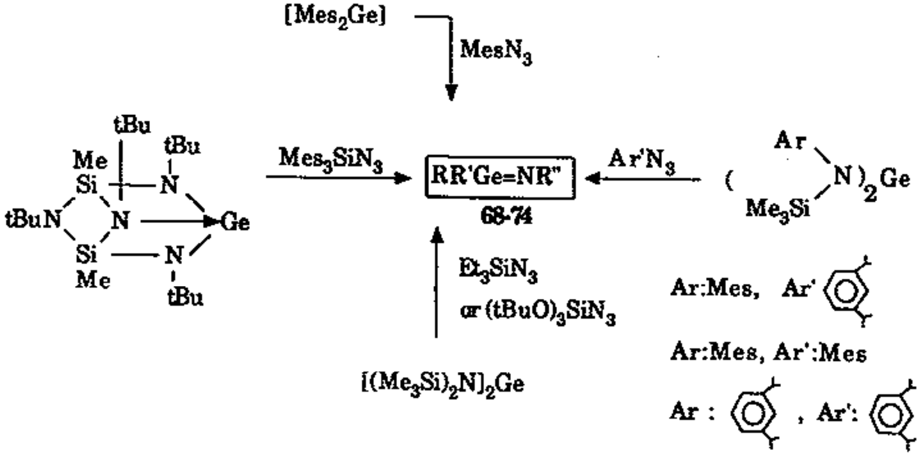
(a) Route a

The first stable germaimine **65** was obtained by Glidewell in the reaction between the electron-rich germylene **66** and the diazo-compound **67** [63,64] (eqn. (45)). Compound **65** exhibits high stability at room temperature in benzene solution, in the absence of air, since addition of EtOH 3 h or 23 h after reaction has minor effect on the yield of adduct. In contrast, when other diazo compounds containing an enolizable function such as $RCH_2COC(N_2)R'$ ($R = H$; $R' = COOEt$, $SO_2C_6H_4$-p-Me, COPh; $R,R' = CMe_2CH_2C(O)–$) are mixed with germylene **66**, the resulting germaimines are not stable [64].

$$\underset{\mathbf{66}}{\mathrm{[(Me_3Si)_2N]_2Ge:}} + \underset{\mathbf{67}}{\mathrm{N_2C(COOMe)_2}} \longrightarrow \underset{\mathbf{65}}{\mathrm{[(Me_3Si)_2N]_2Ge{=}N{-}N{=}C(COOMe)_2}} \qquad (45)$$

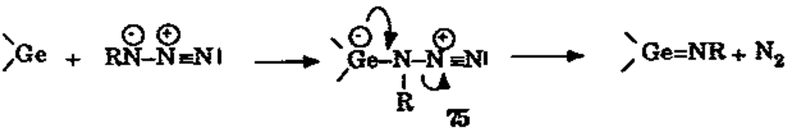
(b) Route b

Reaction of stable germylenes with azides substituted by bulky groups is the best route to stable compounds containing a germanium–nitrogen double bond. Seven stable germaimines **68**, **69** [65] **70–72** [66], **73** [67] and **74** [68] have been obtained by this route in good yields (eqn. (46)) (see Table 3). Although stable germylenes were generally used [65–67], this reaction also occurs with transient dimesitylgermylene generated in situ [68].



(46)

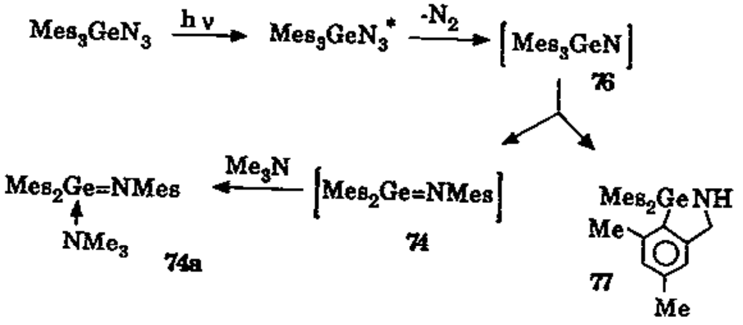
In these reactions, the first step is probably the formation of the intermediate **75** [68] followed by elimination of nitrogen. However such an intermediate has never been observed (eqn. (47)). Germaimines **65**, **68–73** (see Table 3) are stable in solution at room temperature, but **74** must be stabilized by complexation with trimethylamine. When **74** was generated without amine in a benzene or cyclohexane solution, it oligomerized rapidly and could not be chemically characterized.



(47)

(c) Route c

Compound **74** has been obtained through a Curtius type rearrangement by irradiation of Mes$_3$GeN$_3$ [68,69] (eqn. (48)).



(48)

TABLE 3

Germaimines

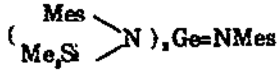
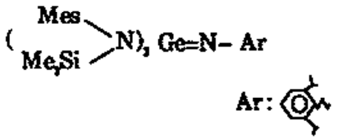
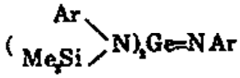
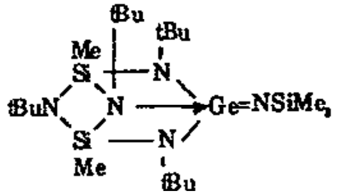
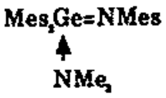
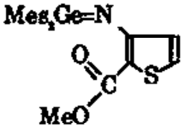
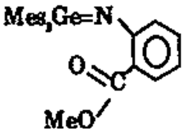
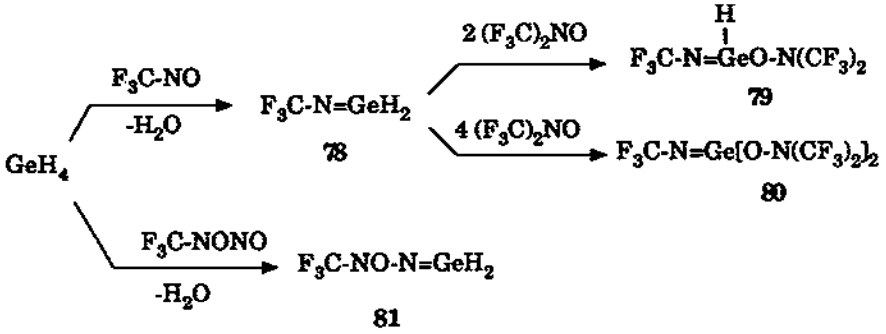
	Germaimines	Synthetic route[a]	d(Ge=N) (Å)	UV λ_{max} (nm)	Ref.
65	$[(Me_3Si)_2N]_2Ge{=}N{-}N{=}C(COOMe)_2$	a	–	502 (C_6H_6) [72] 504 (Et_2O) [72]	63,64
68	$[(Me_3Si)_2N]_2Ge{=}N{-}SiEt_3$	b	–		65
69	$[(Me_3Si)_2N]_2Ge{=}N{-}Si(O^tBu)_3$	b	–		65
70		b	1.691(3)		66
71		b	–		66
72		b	1.703(2)	δ ^{15}N (ratio 2:1): –295, –193	66
73		b	1.688(9)		67
74a	 $\underset{\substack{\uparrow \\ NMe_3}}{Mes_2Ge}{=}NMes$	b c	–	Free 74: 309,459 [69]	68 68,69

TABLE 3 (*continued*)

	Germaimines	Synthetic route[a]	d(Ge=N) (Å)	UV λ_{max} (nm)	Ref.
78	$F_3C–N=GeH_2$	d	–	IR ν(Ge=N) 1030 cm^{-1}	70
79	$F_3C–N=Ge(H)ON(CF_3)_2$	d	–	1028 cm^{-1}	70
80	$F_3C–N=Ge[ON(CF_3)_2]_2$	d	–	1070 cm^{-1}	70
81	$F_3C–NO–N=GeH_2$	d	–		71
82		e	–	325 nm 261 nm	77
83		e			77b

[a] Synthetic routes: (a) coupling between a germylene and a diazomalonic ester; (b) coupling between a germylene and an azide; (c) photolysis of a germylazide; (d) reaction between a germane and a nitroso compound; (e) dehydrochlorination (or fluorination) of a chloro- (or fluoro-) germylamine by tert-butyllithium.

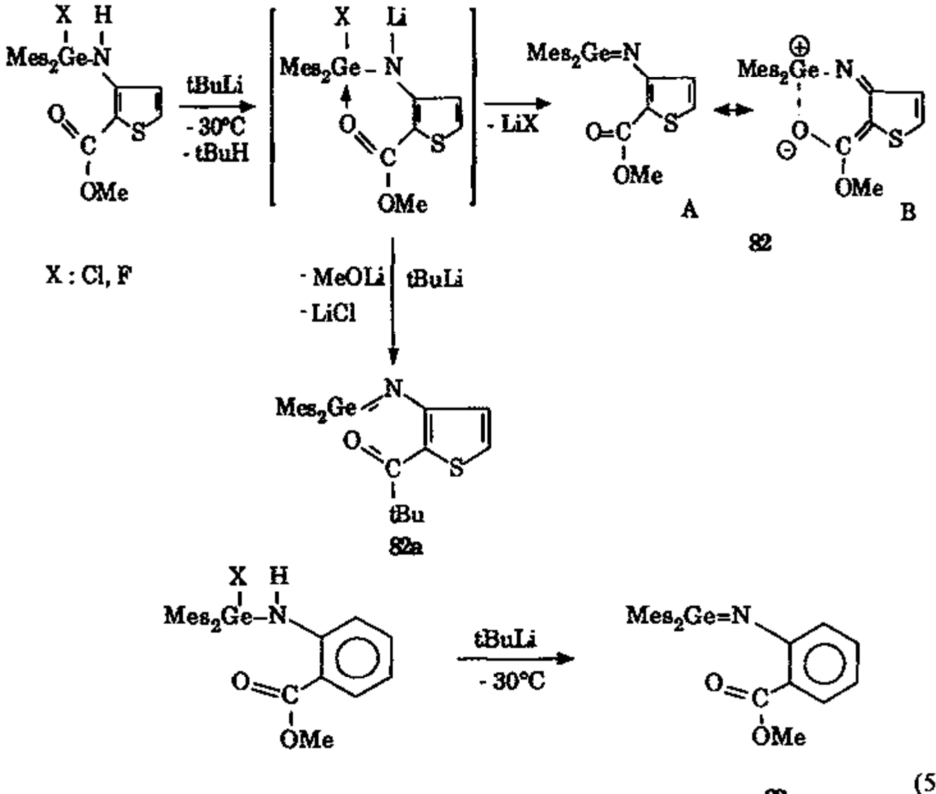
(d) Route d



(49)

A novel synthesis of CF$_3$-bearing germaimines **78–80** [70] and **81** [71] (see Table 3) has been reported in two preliminary publications which appeared 4 years ago (eqn. (49)). Although supporting analytical and spectroscopic data appear to be strong, no comment was made about the astounding resistance of **78** to hydrolysis, unlike all other germaimines. Yet hydrogen iodide added readily. Moreover, the surprisingly high proton chemical shift of the GeH$_2$ group was unexplained even though the value is higher than and inconsistent with those of all other organogermanium compounds. These results are also astonishing since doubly bonded germanium species are usually stabilized by sterically demanding groups. It remains to be seen whether the reported synthesis can be extended to a wider range of germanes and organofluorine compounds. Interestingly, the CF_3 group appears to stabilize compounds having a phosphorus–carbon [73] or a phosphorus–nitrogen [84] double bond.

(e) Route e



82

82a

83 (50)

A new germaimine **82** [77] that is stable in solution at room temperature, has been very recently prepared by dehydrochlorination or dehydrofluorination of the corresponding chloro- (or fluoro)germylamine in excellent yield (nearly 90%) (eqn. (50)). The minor product **82a** (~10%) was obtained when the reaction was performed at room temperature. A similar route leads to stable germylamine **83** [77b] (eqn. (50)). This is the first time that dehydrohalogenation has been used in germaimine synthesis. But, whereas this method is very efficient for germenes >Ge=C< and germaphosphenes >Ge=P–, the dehydrohalogenation of halogermylamines afforded only cyclogermazanes [78a]. When the steric hindrance was important, it appeared very difficult [78b], as also observed in silicon chemistry. In the case of **82**, elimination of halogen is probably easier because of the nucleophilic assistance of oxygen [77]. Germaimine **82** is probably stabilized by conjugation with the thiophoate group, and also by an intramolecular coordination with oxygen of the ester groups as evident from the decrease in the ν(C=O) band in the IR spectrum and the bathochrome shift in the UV spectrum [77]. On this basis, resonance structures **82A** ↔ **82B** can be postulated. Moreover, mesityl groups on germanium appear to be necessary for stabilization since, with ethyl groups, the germaimine was not stable and instead only the corresponding cyclodigermazane was obtained [80].

(ii) Physicochemical studies

(a) X-Ray

Three germaimines have been structurally characterized by X-ray diffraction. The Ge=N double bond lengths: 1.691(3) Å in **70** [66], 1.703(2) Å in **72** [66] (see Fig. 5) and 1.688(9) Å in **73** [67] (see Fig. 6), are in excellent agreement with the calculated value for $H_2Ge{=}NH$ (1.695 Å at the SCF level and 1.727 Å at the CI level) [20]. The bond shortening relative to the standard single bond is about 7.8% . In **70** and **72**, the C–N=Ge–N torsion angles (–1.5(5), 178.4(3)° and –1.5(5), 178.1(3)°, respectively) and the sum of angles at germanium (exactly 360°) are consistent with a normal pπ–pπ double bond.

In compound **73**, the sum of angles at germanium is 357.7° [67], also very close to 360°. From X-ray and NMR data, it seems that it should be described by three resonance structures [67] (eqn. (51)). Apparently, **73** is stabilized by an intramolecular base-stabilization, a new concept which appears to be very efficient and does not affect the reactiv-

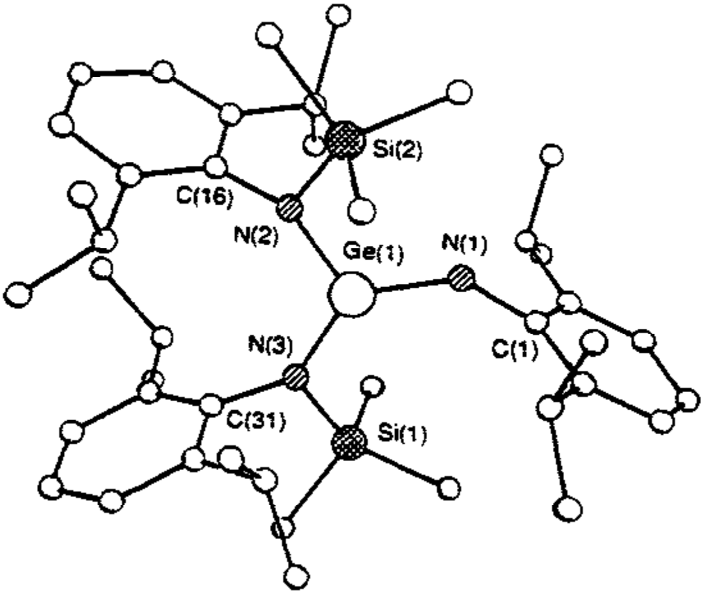


Fig. 5. Molecular structure of **72** (reprinted from J. Chem. Soc. Chem. Commun., (1991) 1123).

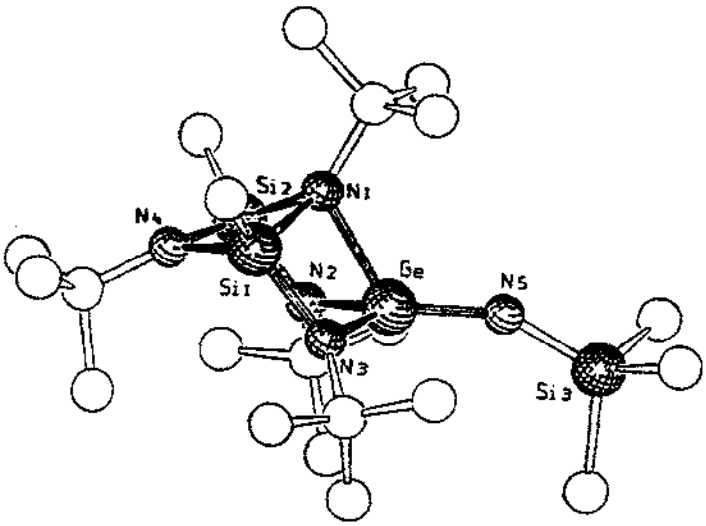
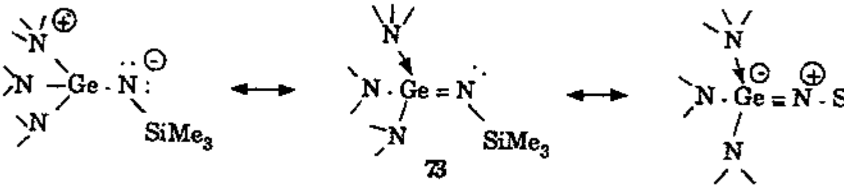


Fig. 6. Molecular structure of **73** (reprinted from Angew. Chem. Int. Ed. Engl., 29 (1990) 216).

ity of the germaimine. A similar stabilization by intramolecular coordination with a nitrogen occurs in silaimines >Si=N– [74] and silaphosphenes, >Si=P– [74], but in these cases, the Si=N(P) double bond is unreactive.

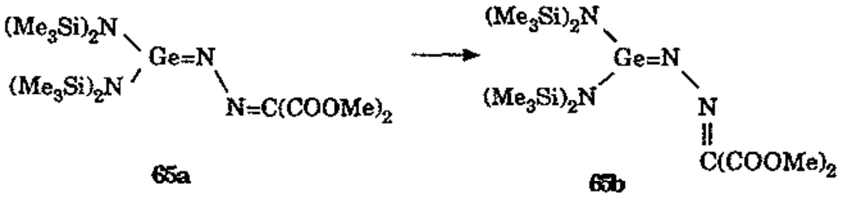


(51)

(b) Theoretical studies

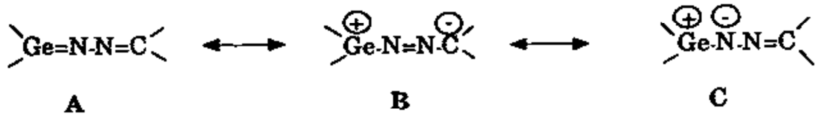
Germaimine $H_2Ge{=}NH$ was predicted to be planar [20]. The calculated geometry and the Ge=N bond distances agree well with the experimental values [66,67]. The charge distribution shows a very polar bond (Ge, +0.54; N, –0.70 [20]) and a large dipole moment (2.99 D).

Compound **65** slowly changes over a period of a few days into a second species. The similarities between the NMR spectra of the two compounds show that they are isomeric. The initial form is the transoïd **65a**, and the more stable the cisoïd **65b** [63,72] (eqn. (52)).



(52)

These results have been confirmed by MNDO calculations on the simpler analogue $[(H_3Si)_2N]_2GeNN(COOMe)_2$ [72]. Structural data suggest that **65** should be represented as a hybrid of three forms, with C as the most important contributor [72] (eqn. (53)).



(53)

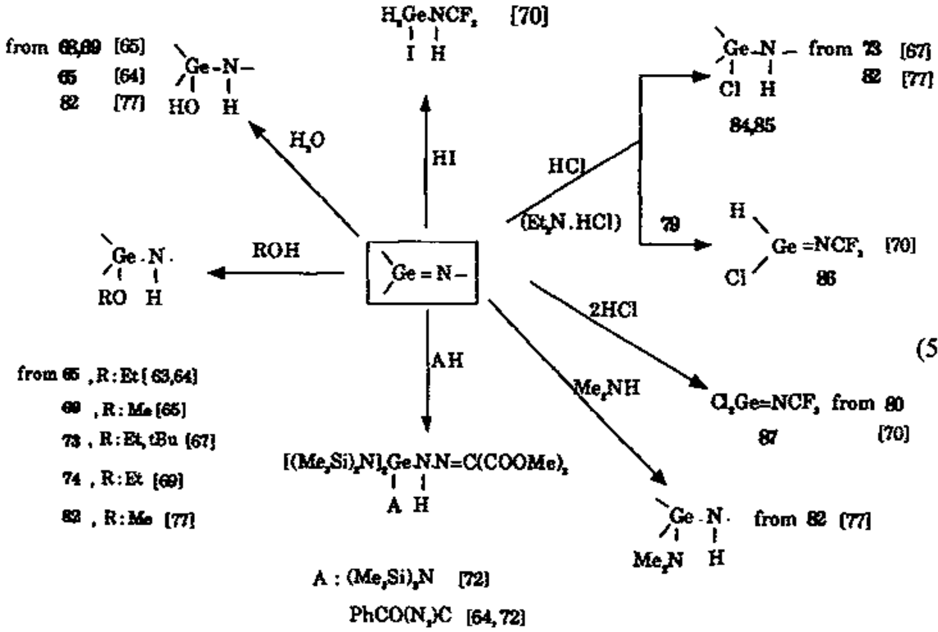
(c) IR, UV, NMR

The Ge=N stretching vibration has been observed experimentally at 1028 (**79**), 1300 (**78**) and 1070 cm^{-1} (**80**) [70]. It was one of the most important physicochemical data responsible for the characterization of germaimines **78–80** [70]. These values are slightly higher than previously reported for $F_2Ge{=}NPh$ (970 cm^{-1} [la]) and much higher than calculated (854 cm^{-1} [20]). In the UV spectra, bands were observed at 502 nm (in Et_2O) and 504 nm (in C_6H_6) for **65** [72]. In the case of **74**, two bands were observed at 459 nm ($n \rightarrow \pi^*$) and 309 nm ($\pi \rightarrow \pi^*$) [69]. These measurements were done in an argon matrix since **74** is only stable at room temperature when it is complexed by an amine. In the ^{15}N NMR spectrum of **72**, two signals were observed in the ratio 2:1 at –295 and –193 ppm, respectively, for the three nitrogen atoms [66].

(iii) Reactivity

(a) Protic reagents

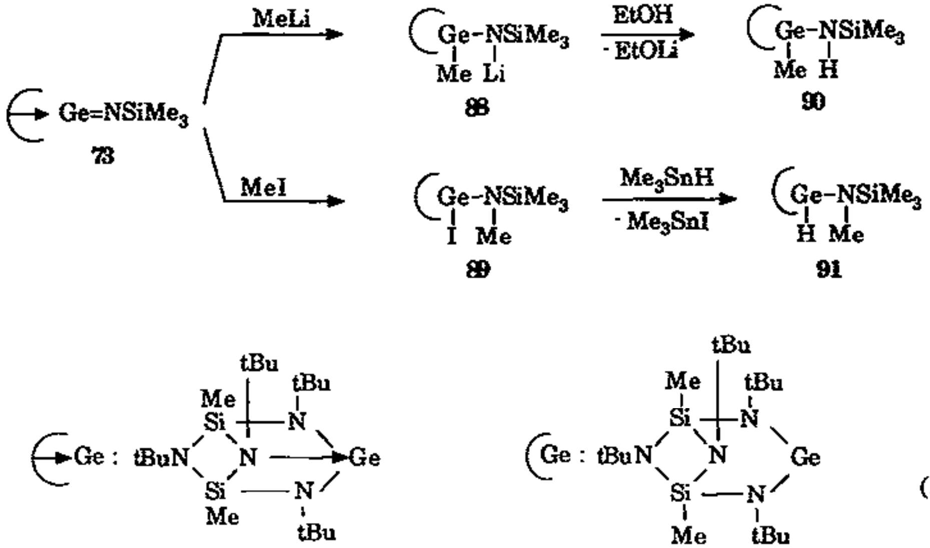
Whereas the reactivity of transient germaimines is now well known [4 and refs. therein], the chemical behavior of stable germaimines is still relatively undeveloped. Most characterization reactions have been done with protic reagents (alcohols, water, mineral acids) or compounds with active hydrogen ($(Me_3Si)_2NH$, $PhCOCH(N_2)$) (eqn. (54)). The reactions displayed in eqn. (54) deserve some comment. They occur regiospecifically, with hydrogen always on nitrogen, and usually in excellent yield. In the case of hydrochloric acid, addition to the Ge=N double bond is normally observed in **73** and **82**, giving **84** [67] and **85** [77], respectively. In contrast, a rather surprising reaction occurs between HCl and **79** or **80**; cleavage of the Ge–O bond is observed, leading only to the corresponding chlorogermaimines **86** and **87** in 53 and 57% yield, respectively, together with an almost quantitative yield of bis(trifluoromethyl)hydroxylamine. These new germaimines are stable at –20°C. In some cases the labile Ge–N bond is cleaved by an excess of protic reagent, leading to dimesityldiethoxygermane (e.g. **74** with EtOH [69]) or germoxane ($([(Me_3Si)_2N]_2GeO)_n$ (e.g. **65** with H_2O [64,72]). Similar results are obtained when EtOH is added to **65** 3 h or 23 h after its synthesis; the yield decreases only from 83 to 75%, indicating a considerable lifetime at room temperature for this germaimine.



(54)

(b) Lithio compounds and methyliodide

Methyllithium and methyliodide add to the double bond of **73** with the electropositive part of the reactant bound to nitrogen and the electronegative part on the germanium atom as expected. Quenching **88** with ethanol, and addition of trimethylstannane to **89** yield the two regioisomers **90** and **91**, respectively. Such reactions are interesting since they give two compounds which differ only in the position of the hydrogen atom and methyl group on germanium and nitrogen [75] (eqn. (55)).

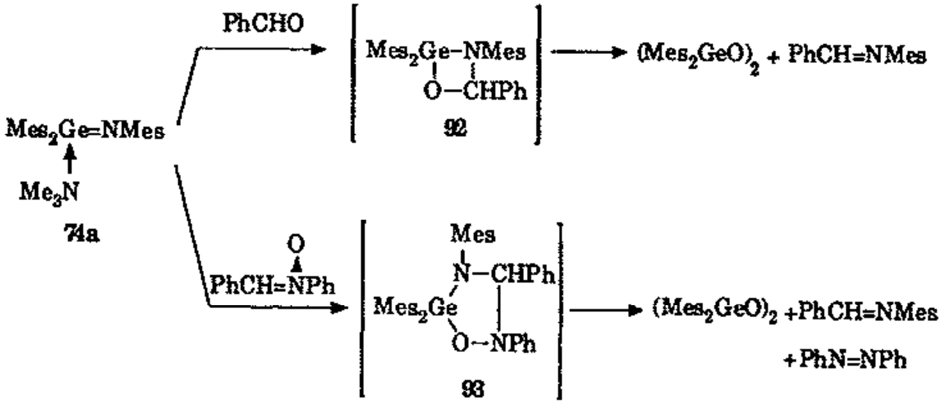


(55)

Addition of methyliodide to the Ge=N double bond of **73** shows the high reactivity of such a derivative, although the germanium is complexed with nitrogen. Note that such addition of alkyl iodide to a stable doubly bonded germanium species has never been observed before.

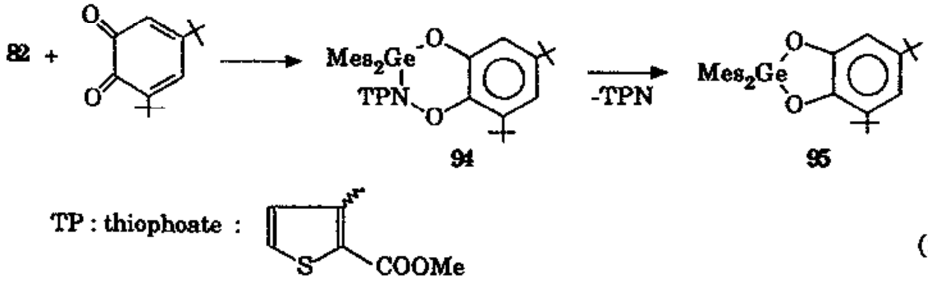
(c) Cycloadditions

The free transient germaimine $Mes_2Ge{=}NMes$ **74** can be characterized by trapping with benzaldehyde during the course of the irradiation of Mes_3GeN_3. But if benzaldehyde is added after the end of the irradiation, no pseudo-Wittig reaction occurs, showing that free **74** is not stable at room temperature [68]. When the irradiation was done in the presence of trimethylamine, the complexed germaimine **74a** showed good stability, since addition of benzaldehyde or diphenylnitrone gave the expected pseudo-Wittig reaction even after the end of the irradiation [68] (eqn. (56)).



(56)

These reactions involve the intermediate formation of four- and five-membered ring derivatives **92** and **93** which are not stable and give the classical decomposition of cycloadducts of germaimines [76]. A [2+4] cycloaddition has been observed between germaimine **82** and 3,5-di-tert-butyl-*ortho*-quinone, leading to cycloadduct **94** [77], then to the corresponding germadioxolane **95** according to a type of decomposition already observed in derivatives having similar structure [81] (eqn. (57)).



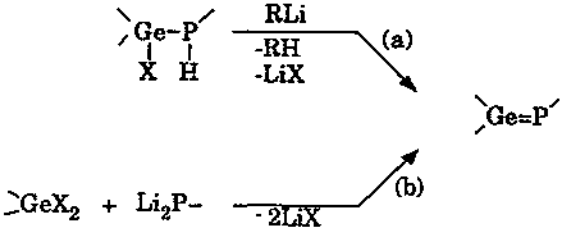
(57)

E. GERMAPHOSPHENES >Ge=P–

(i) Synthesis

Stable germaphosphenes are obtained in two ways (eqn. (58)):

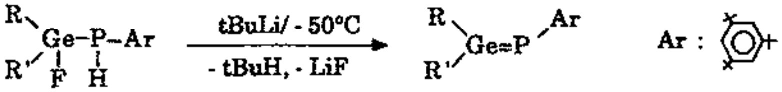
dehydrohalogenation of halogermylphosphines by tert-butyllithium (route a);
synthesis in one step by reacting dihalogermanes with dilithiophosphides (route b).



(58)

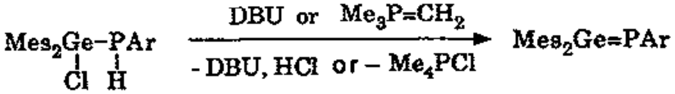
(a) Route a

The dehydrofluorination of the corresponding fluoro precursor by tert-butyllithium is the best route to germaphosphene **96** [82], **97**, **98** [83] and **99** [83], which are all obtained nearly quantitatively (eqn. (59)). In dehydrohalogenation reactions, the best results are obtained with fluoro-germanium derivatives. Owing to the high germanium–fluorine bond energy (113 kcal/mol) [12], the Li/halogen exchange frequently observed when germanium is substituted by other halogens, does not occur. Moreover, bulky lithio compounds such as ^{t}BuLi prevent direct alkylation of germanium. Note that silaphosphenes >Si=P– are usually obtained from chloro precursors [85–87], and rarely from fluoro precursors [88]. Germaphosphene **96** can also be prepared by dehydrochlorination of the corresponding chlorogermylphosphine by trimethylmethylenephosphorane [82] or DBU [82], but in low yields. These are only marginal routes to germaphosphenes (eqn. (60)).



(59)

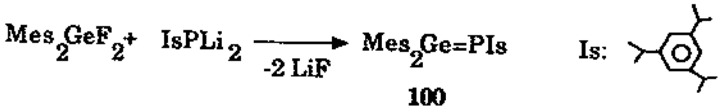
R, R' : Mes, **96** ; tBu **99**
R : Mes, R' : tBu ; **97**,**98**



$$\underset{\mathrm{Cl}\ \ \mathrm{H}}{\mathrm{Mes_2Ge{-}PAr}} \xrightarrow[\text{- DBU, HCl or} - \mathrm{Me_4PCl}]{\text{DBU or } \mathrm{Me_3P{=}CH_2}} \mathrm{Mes_2Ge{=}PAr} \qquad (60)$$

(b) Route b

The germaphosphene **100** [89] can be synthesized in a one-step reaction between dimesityldifluorogermane and 2,4,6-tri-isopropylphenyldilithiophosphide, which is obtained from the corresponding phosphine and 2 equiv. of butyllithium. This type of process, generally less clean than the two-step reaction, gave good results for **100** (eqn. (61)).



$$Mes_2GeF_2 + IsPLi_2 \xrightarrow[-2\,LiF]{} Mes_2Ge{=}PIs \qquad Is:$$

100

(61)

(ii) Physicochemical studies

(a) X-Ray diffraction

The presence of a double bond between germanium and phosphorus was proved unambiguously by an X-ray crystal structure determination. In the cases of **96** (2.138 Å) [91] (Fig. 7) and **98** (2.14 Å) [83] (Fig. 8), a shortening of about 8–9% compared to the Ge–P single bond (2.33–2.36 Å for a single bond [92]) was observed. This is typical for organometallic doubly bonded compounds. Moreover, **96** and **98** adopt a nearly planar conformation of the central atoms $C_2Ge{=}PC$ with the sum of angles on germanium practically 360°. The Ge=P bond length is in good agreement with calculated values by Barthelat [93] of 2.169 Å at the SCF level with configuration interactions, and 2.136 Å by ab initio calculations using pseudopotentials. These calculations also agree well with the sum of covalent radii (2.12 Å) of sp^2 hybridized germanium (1.12 Å) and sp^2 phosphorus (1.00 Å).

(b) Isomerization barrier

As mentioned above, dehydrofluorination of fluorogermylphosphine **101** afforded germaphosphenes **97** and **98** [83]. However, only the isomer with a *cis* arrangement of Mes and Ar groups (**97**) is observed immediately after the reaction, even when starting

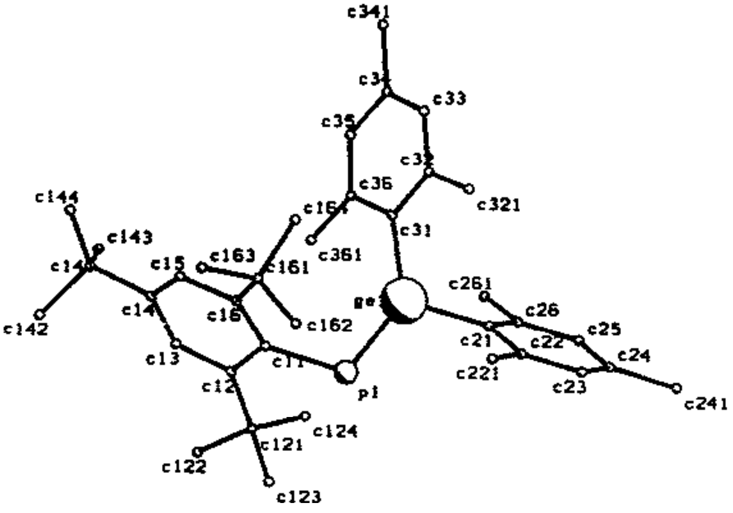


Fig. 7. Molecular view of **96** (reprinted from Organometallics, 7 (1988) 1010)

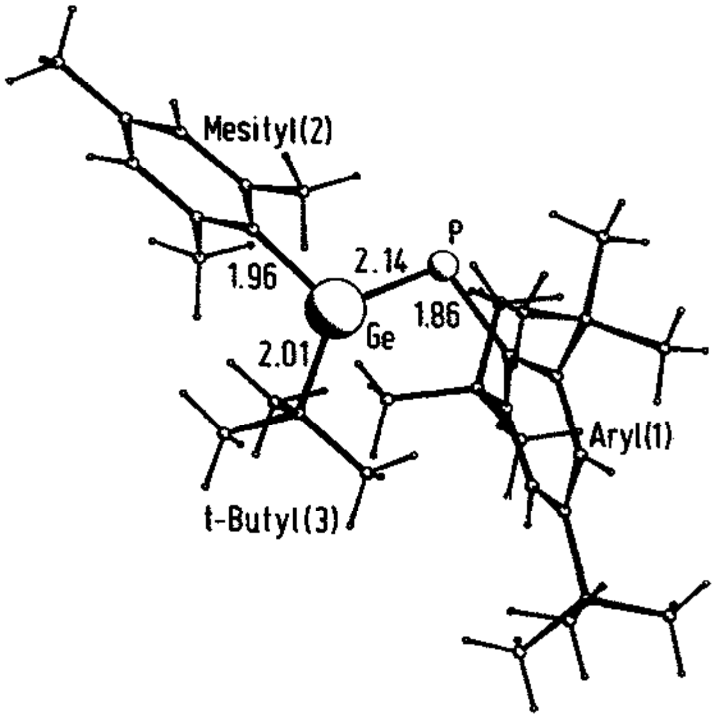
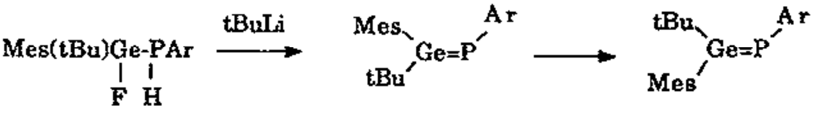


Fig. 8. Molecular view of **98** (reprinted from New J. Chem., 13 (1989) 389).

with a 60:40 mixture of the two diastereoisomers **101a/101b** (eqn. (62)). This phenomenon can be explained by the preferential reaction of one of these two diastereoisomers, followed by a rapid thermodynamic equilibrium between them, probably due mainly to the high configurational instability of asymmetric fluorogermanes [90]. After 5 h at room temperature, complete isomerization of **97** to **98** was observed [83] (eqn. (62)). Both isomers were identified by NMR spectroscopy, and **98** also by X-ray diffraction (see Section (E(ii)(a)).



$$\underset{\mathbf{101}}{\mathrm{Mes(tBu)Ge(F)\text{-}P(H)Ar}} \xrightarrow{\mathrm{tBuLi}} \underset{\mathbf{97}}{\mathrm{(Mes)(tBu)Ge{=}PAr}} \longrightarrow \underset{\mathbf{98}}{\mathrm{(tBu)(Mes)Ge{=}PAr}} \qquad (62)$$

101 **97** **98**

The *cis-trans* isomerization barrier **97** ⇌ **98** (22.3 kcal/mol) has been determined by NMR spectroscopy. A similar value (20.3 kcal/mol) was obtained for the diphosphene ArP=PAr (Ar: 2,4,6-tri-tert-butylphenyl) [94]. The *cis* arrangement of Ar and ^{t}Bu may seem surprising since tert-butyl is considered to be bulkier than mesityl [95]. However, free rotation of all groups is not possible when mesityl and Ar are *cis*.

(c) NMR and Raman spectra

Germaphosphenes display characteristic low field ^{31}P NMR signals (between +145 and +173.6 ppm; see Table 4) [82,83,89]. A rather large temperature dependence has been observed for the δ^{31}P [83] with increasing temperature effecting a low field shift, up to 12 ppm, between −80°C and +80°C (see Table 4). This corresponds to a red shift in the electronic absorption spectrum. As a result, germaphosphenes display high thermochromism, yellow at −80°C, orange at room temperature, and orange-red at +80°C. Such a reversible phenomenon has previously been noted in other doubly bonded species like disilenes [17] and diphosphenes [19], and similar relationship between electronic absorption and ^{119}Sn chemical shifts is observed in the series $Ph_3Sn(Sn^tBu_2)_nSnPh_3$ ($n = 1$–4) [96]. Germaphosphenes **96** and **98** have strong Raman emission bands at 503 and 501.5 cm^{-1}, respectively (see Table 4) [83]. A good correlation is observed with previous calculations: 481 cm^{-1} [93] using pseudopotentials and configuration interactions.

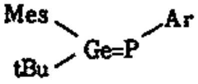
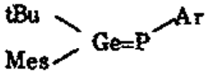
(iii) Reactivity

(a) Protic reagents

Orange solutions of germaphosphenes **96–100** are extremely air- and moisture-sen-

TABLE 4

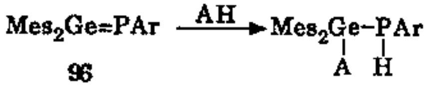
Germaphosphenes

	Germaphosphenes	Synthetic route[a]	Raman (cm^{-1})	δ ^{31}P (ppm)	d(Ge=P) (Å)	Ref.
96	$Mes_2Ge{=}PAr$	a	503	+173.6 (+164.8: −80°C +178.2: +80°C)	2.139(3) [91]	82 91
97		a	–	+169.2		83
98		c	501.5	+157.4 (+149.1: −80°C +161.0: +80°C)	2.14(4)[b] 2.14(3)	83
99	$^tBu_2Ge{=}PAr$	a	–	+156.6 (+148.5: −80°C +159.8: +80°C)		83
100	$Mes_2Ge{=}PIs$	b	–	+146.8		89

[a] (a) Dehydrofluorination by ^{t}BuLi of a fluorogermylphosphine; (b) one step process: reaction of difluorodimesitylgermane with a dilithiophosphide; (c) isomerization from another germaphosphene.

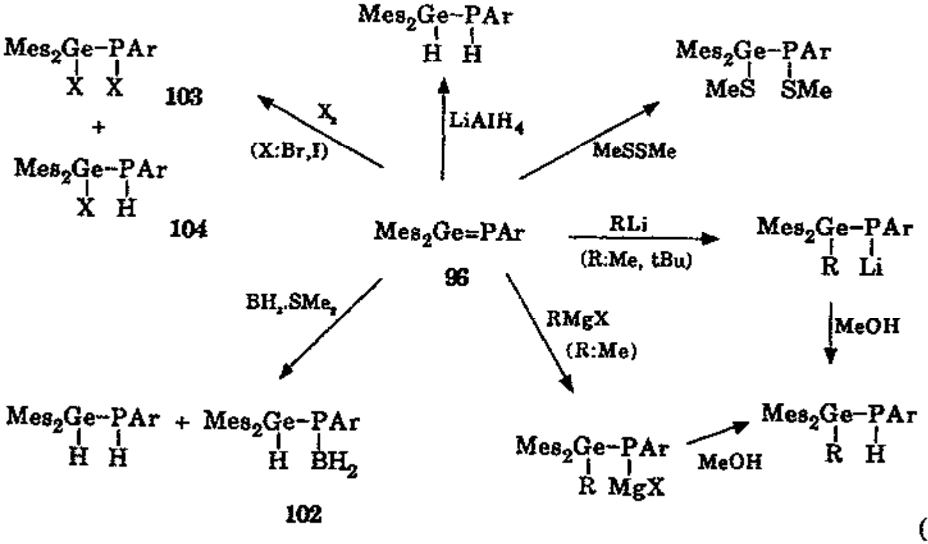
[b] Two crystallographic independent molecules.

sitive, but they can be stored without change for months in an inert atmosphere. They behave only as doubly bonded compounds, never as germylene R_2Ge or phosphinidene RP should the germanium–phosphorus connection be very weak. Germaphosphene **96** reacts quantitatively with protic reagents or compounds with active hydrogen, such as phenylacetylene or trimethylmethylenephosphorane (eqn. (63)) [82,97–99]. These reactions are regiospecific, giving only secondary phosphanes. The regiochemistry is determined primarily by polar effects since the germanium–phosphorus bond is slightly polarized $Ge^{\delta+}{=}P^{\delta-}$. Addition of water or hydrofluoric acid to **98** gives a mixture of two diastereoisomers Mes(^{t}Bu)(A)GeP(H)Ar (A = F or OH) due to a rapid thermodynamic equilibrium [83].



$$\underset{\mathbf{96}}{Mes_2Ge{=}PAr} \xrightarrow{AH} Mes_2\underset{A}{Ge}{-}\underset{H}{P}Ar \qquad \begin{array}{l} A: Cl, F, HO, MeO, PhNH, \\ iPrS, CH_3COO, Ph{\equiv}C, \\ Me_3P{=}CH \end{array} \tag{63}$$

(b) Lithio compounds, Grignard reagents, hydrides, disulfides, halogens and carbon tetrachloride

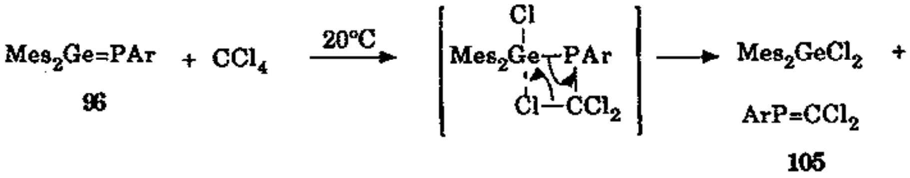


(64)

Germaphosphene **96** is highly reactive towards nucleophiles. Methyllithium, tert-butyllithium and methylmagnesium iodide react rapidly at room temperature to give, after methanolysis, the corresponding secondary phosphanes [97,99] (eqn. (64)), and the reactions are all regiospecific. Lithium aluminium hydride reduces the germanium–phosphorus double bond [97,99], as do boranes such as $BH_3 \cdot SMe_2$. In this case, the adduct **102** was also observed in minor quantities [97] (eqn. (64)) depending on experimental conditions. Germaphosphene **96** reacts with dimethyldisulfide, probably by a radical process [97,99]. Each reaction involves only the germanium–phosphorus double bond. The Ge–P single bond, which is usually cleaved by lithio compounds [100], Grignard reagents [101] and hydrides [102], is unaffected due to large steric hindrance by mesityl and tri-tert-butylphenyl groups .

Halogens react with **96** to produce the expected adducts **103** and, surprisingly, halogermylphosphines **104** as major products [97,99] (eqn. (64)). Two competitive mechanisms probably occur, an electrophilic addition leading to **103** and a radical process forming the radical $Mes_2Ge(X)–P^{\cdot}Ar$ which reacts further with halogen, or by hydrogen abstraction to produce either **103** or **104**.

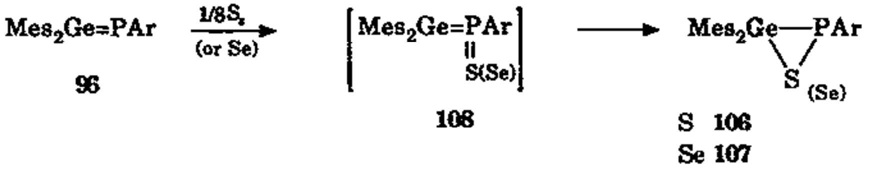
The reaction of **96** with carbon tetrachloride is particularly interesting because it allows the quantitative synthesis of a compound with a phosphorus–carbon double bond **105** from a compound having a germanium–phosphorus double bond [97] (eqn. (65)).



(65)

(c) [2+1] Cycloadditions

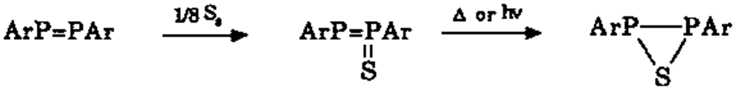
Reaction of an equivalent sulfur or selenium with germaphosphene **96** leads to stable three-membered heterocycles, the germathiaphosphirane **106** and the germaselenaphosphirane **107** [103] (eqn. (66)). The first step of the reaction is probably the formation of the germaphosphene sulfide (or selenide) **108** followed by its isomerization to the three-membered ring. A similar process has been demonstrated by Yoshifuji in the reaction of sulfur with a diphosphene [104] (eqn. (67)). The X-ray crystal structure of **106** is rather surprising since germanium, phosphorus and the three ipso carbons of the aromatic rings are nearly in a plane as in the starting germaphosphene. Moreover, the germanium atom is nearly planar (sum of angles 358.1°) with respect to the two mesityl groups and the P atom, and the germanium–phosphorus bond is shorter than a classical Ge–P single bond (2.316 Å versus 2.35–2.36 Å) [92]. Apparently the hybridization of germanium is between sp^2 and sp^3 and the bonding intermediate between a normal three-membered ring and a π-complex (eqn. (68)).



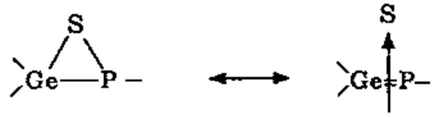
(66)

Similar observations have been reported by West for disilaoxiranes

Si–Si–O [105] and disilathiiranes Si–Si–S [106] in which the Si–Si bonds are shorter than expected with quasi planar silicon atoms. This hypothesis is supported by a theoretical investigation of three-membered rings containing two silicon atoms [107]. The same phenomenon has been described for other three-membered ring derivatives (see Section C2).



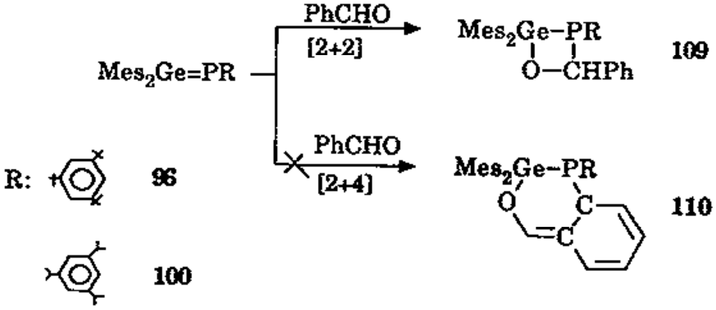
(67)



(68)

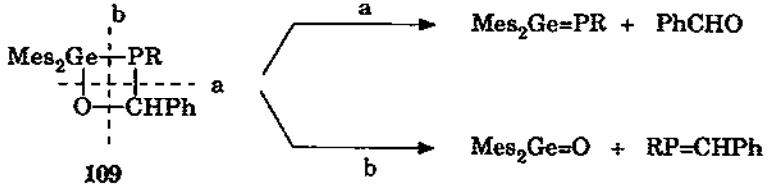
(d) [2+2] Cycloadditions

Germaphosphenes **96** and **100** react readily with benzaldehyde by [2+2] cycloaddition to give the corresponding four-membered ring heterocycles **109** [89] (eqn. (69)).



(69)

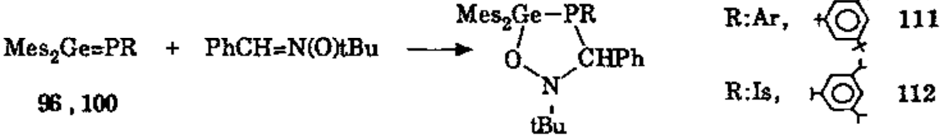
The first step of this reaction is probably the nucleophilic attack of oxygen on germanium, followed by cyclization. Although the Ge–P bond is only slightly polarized, a regioselective reaction takes place with oxygen bonded exclusively to germanium. Six-membered ring heterocycles such as **110** are never obtained, contrary to [2+4] cycloadditions reported between benzophenone and some transient germenes Ge=C [28] or silenes Si=C [108]. The ^{31}P NMR signal of **109** appears at low field (between +45 and +82 ppm depending on group R on phosphorus). Such a large deshielding has been explained by folding of the four-membered ring allowing an interaction between phosphorus and oxygen lone pairs [89]. In the mass spectrum of **109**, the classical [2+2] decomposition of organometallic four-membered ring heterocycles has been observed, the most important route a (a/b 95:5) regenerating the starting material [89] (eqn. (70)).



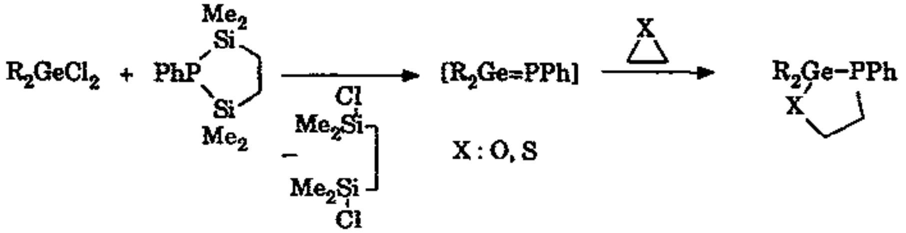
(70)

(e) [2+3] Cycloadditions

Reactions of α-phenyl-N-tert-butylnitrone with germaphosphenes **96** and **100** afford the corresponding five-membered ring heterocycles **111** and **112** [89] (eqn. (71)). Whilst two diastereoisomers were obtained for **112**, only one was observed for **111**, probably due to the large steric hindrance imposed by the 2,4,6-tri-tert-butylphenyl group. An insertion with ring expansion, equivalent to a [2+3] cycloaddition, involving oxirane or thiirane, was the first method of characterization of transient germaphosphenes obtained by dechlorosilylation reactions between dichlorogermanes and disilylphosphines [109] (eqn. (72)).



(71)



(72)

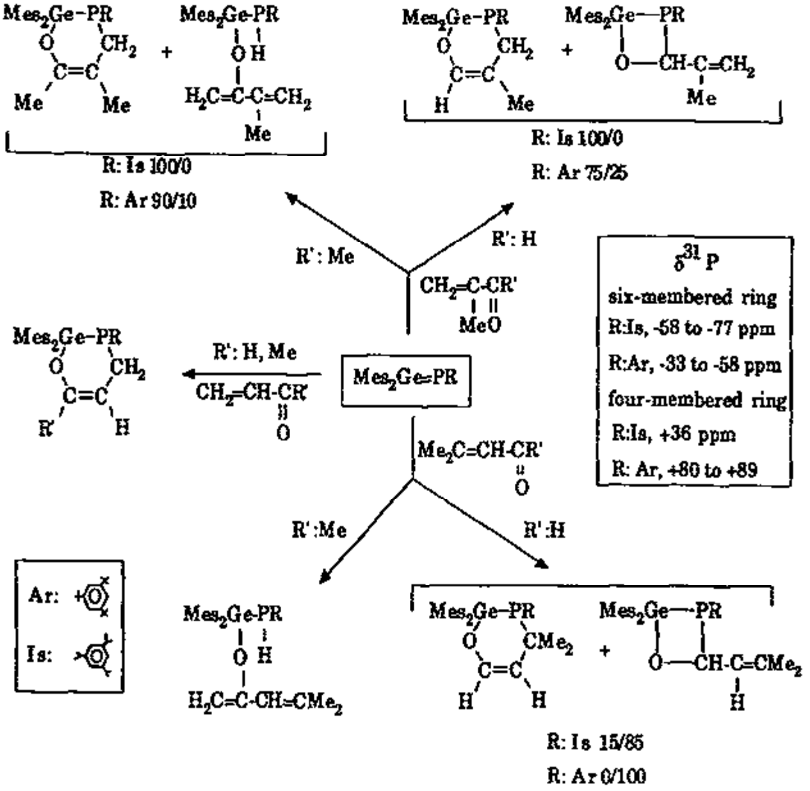
(f) [2+4] Cycloadditions

Germaphosphenes **96** and **100** react with α-ethylenic aldehydes and ketones to produce six-membered ring germaoxaphosphorinenes according to a [2+4] cycloaddition [110]. However, four-membered ring compounds ([2+2] cycloaddition) and open-chain products are also obtained with α or β methyl-substituted aldehydes and ketones, respectively (eqn. (73)). Hence, it seems that the outcome of the reaction strongly depends upon steric hindrance, both on the carbonyl compound and on the germaphosphene. The first step of these reactions is probably the nucleophilic attack of oxygen on the germanium centre while the attack of phosphorus occurs at the carbonyl carbon or the β carbon, depending on the substituents on these atoms.

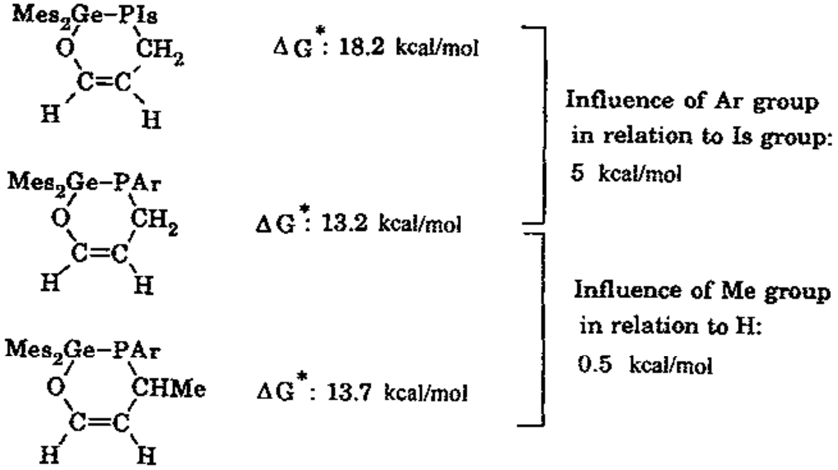
Four- and six-membered ring derivatives are easily differentiated in ^{31}P NMR spectra by their very different chemical shifts (−33 to −77 ppm for six-membered rings, +36 to +89 ppm for four-membered rings) [110].

The inversion barrier of phosphorus has been determined for three derivatives [110] (eqn. (74)). These low barriers are due to the substitution of phosphorus by the electropositive germanium (electronegativity 2.0) and particularly by the large steric effects of the substituted aromatic rings. Such studies have determined the influence of the aryl group bonded to phosphorus (Ar in relation to Is) and of the substitution on the 4-carbon of the carbonyl (Me in relation to H).

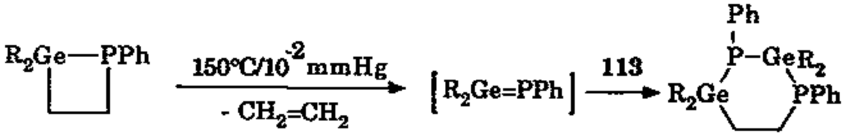
Interestingly an insertion with ring expansion, equivalent to a [2+4] cycloaddition, has previously been observed with germaphosphenes obtained by thermolysis of four-membered rings. This was, for a long time, practically the only evidence for the formation of transient germaphosphenes [114] (eqn. (75)).



(73)



(74)

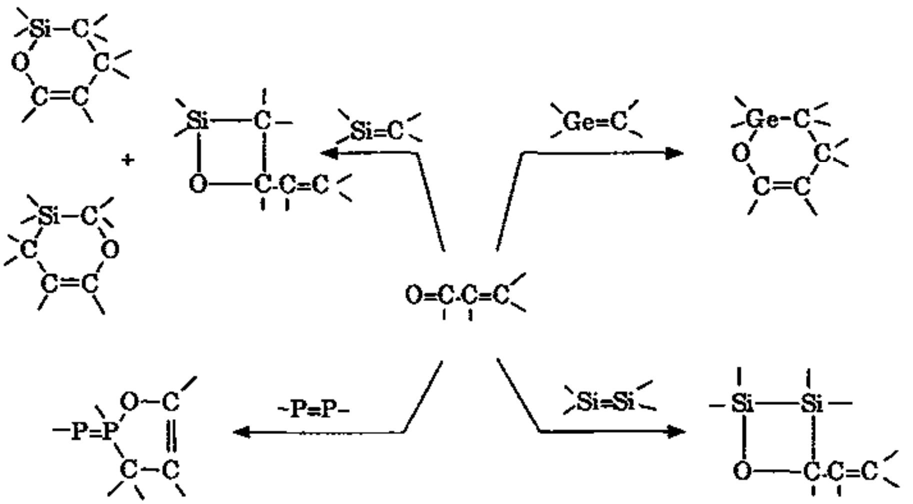


113

(R: Me, Et)

(75)

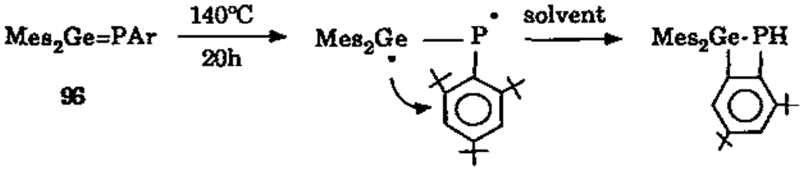
Various types of cycloadditions have been observed between α-ethylenic aldehydes and ketones and other doubly bonded main group elements including exclusive [2+2] cycloadditions with disilenes [111], [2+4] with germenes [25], [2+2] and [2+4] with silenes [112]. With diphosphenes a cycloaddition involving one of the phosphorus atoms was observed to give a five-membered ring [113] (eqn. (76)).



(76)

(g) Thermolysis

Heating **96** at 140°C affords the stable germaphosphetene **114** [115] (eqn. (77)) probably by an intramolecular radical aromatic substitution. Compound **114** is the first heterocycle of this type to be prepared and has been structurally characterized. Although the four-membered ring is highly strained, it is thermally stable.



96

114

(77)

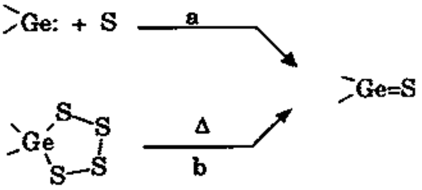
Of the silaphosphenes, >Si=P–, germaphosphenes >Ge=P– and stannaphosphenes >Sn=P– series, the germaphosphenes have been the most extensively studied. This is probably due to their straightforward synthesis allowing the isolation of pure crystalline derivatives. The germanium–phosphorus double bond appears very reactive in spite of the large steric hindrance necessary for its stabilization.

F. GERMATHIONES >Ge=S

(i) Synthesis

Stable germathiones are obtained by two routes (eqn. (78)):

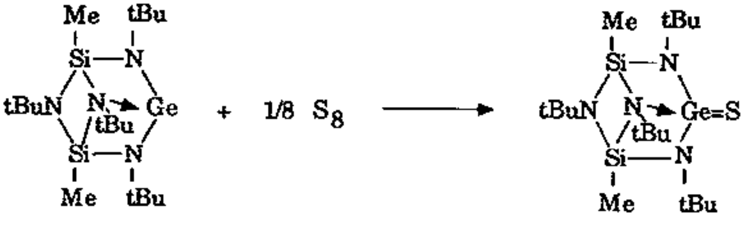
- coupling of a germylene with sulfur (route a);
- decomposition of a germatetrathiolane (route b).



(78)

(a) Route a

The germathione **115** is obtained in high yield by a reaction between the stable germylene **116** and sulfur [116] (eqn. (79)). All previous attempts to isolate germathiones failed even with sterically demanding ligands on the germanium, and compound **115** is the first derivative with a base-stabilized double bond between sulfur and germanium. Stabilization of a doubly bonded compound of the type $>Ge{=}M_{16}$ (M_{16} = O, S, Se) is of course much more difficult than the stabilization of compounds such as $>Ge{=}M_{15}$ (M_{15} = N, P) or $>Ge{=}M_{14}$ (M_{14} = C, Ge) since there is no substituent on the M_{16} element. Therefore complexation of germanium by a Lewis base is advantageous. A similar stabilization allowed the isolation of a stable compound with a silicon–sulfur double bond [117].



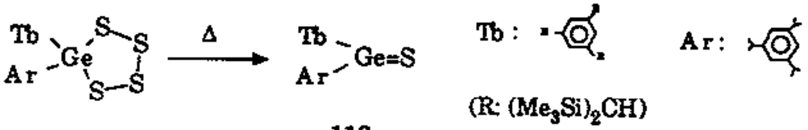
116 **115**

(79)

By contrast with sulfur, the reaction of germylene **116** with oxygen did not afford stable germanone >Ge=O, but only its dimer [116].

(b) Route b

Recently, Tokitoh obtained the new stable germathione **118** by thermolysis of the germatetrathiolane **117**. Compound **118** is stabilized by the extremely bulky substituents on germanium (eqn. (80)) [121].



117 **118**

(80)

(ii) Physicochemical studies

(a) X-Ray diffraction

The geometry of germanium in **115** can be described as trigonal-planar (GeSN^{4}N^2) with an additional bond (GeN^3) since the sum of angles on germanium deviates by only 5° from the ideal value of 360° [116]. The Ge–S bond length (2.063(3) Å) is the shortest germanium–sulfur bond observed, 0.2 Å shorter than that of a single bond [118] (Fig. 9). Theoretical calculations predict the Ge=S double bond length to be 2.02 Å in $H_2Ge{=}S$ [119] (using pseudopotentials or MNDO methods) and 2.01 Å in $Me_2Ge{=}S$ [120] (ab initio Hartree–Fock level calculations). On the basis of X-ray and NMR measurements, it seems that **115** can be formally described in terms of the two resonance structure **115a** and **115b** [67] (eqn. (81)).

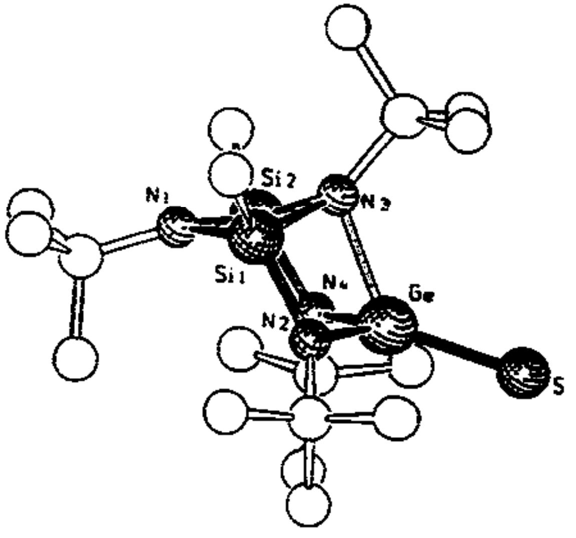
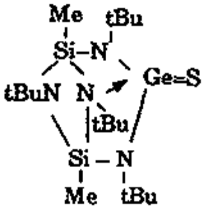
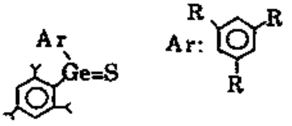


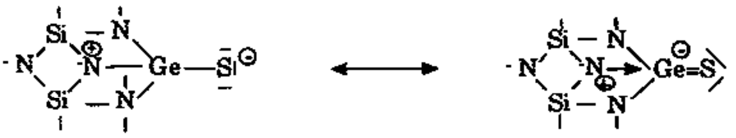
Fig. 9. Molecular view of **115** (reprinted from Angew. Chem. Int. Ed. Engl., **28** (1989) 1237).

TABLE 5

Germathiones

		Synthetic route[a]	d(Ge=S) (Å)	Ref.
115		a	2. 063 (3)	116
118	 (R:$(Me_3Si)_2CH$))	b		121

[a] (a) Reaction of a stable germylene with sulfur; (b) decomposition of a germatetrathiolane.



115 a **115 b**

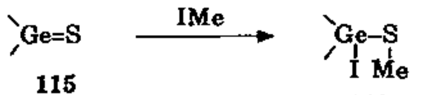
(81)

(b) IR spectra

The only IR spectrum of a germathione obtained to date is that for transient $Me_2Ge{=}S$ trapped in an argon matrix at 18–20 K. The observed Ge=S stretching vibration (604.6 cm^{-1}) is in good agreement with calculated values (666 cm^{-1} [119] and 586 cm^{-1} [Ia]).

(iii) Reactivity

The reactivity of transient germathiones is well known (see [4] and refs. therein). But, for the recently prepared stable germathione **115**, only the addition of methyl iodide to the germanium–sulfur double bond has been studied [75] (eqn. (82)). In the adduct **119**, iodine is bound to germanium and the methyl group to sulfur, as expected from the bond polarity $Ge^{\delta+}{=}S^{\delta-}$. This reaction shows that the base-stabilized germathione **115** behaves as a normal unsaturated molecule.



115 **119**

(82)

G. CONCLUSION

Great progress has been made in the field of organogermanium doubly bonded species in the 1980s and the beginning of the 1990s during which more than 30 stable germenes, digermenes, germaimines, germaphosphenes and germathiones have been synthesized and isolated. These compounds are stabilized by various means, the most important being the use of very bulky substituents which prevent their oligomerization. However, electronic effects, such as conjugation, also play a role, especially in germenes and germaimines. In the last case, the powerful –I effect of CF_3 attached to nitrogen probably allowed the extraordinary stabilization of germaimines substituted by small groups. The intermolecular or intramolecular base stabilization (by oxygen or nitrogen) also appears to be an effective way to stabilize germaimines.

Some doubly bonded germanium species have been structurally characterized by single crystal X-ray diffraction, showing germanium to be planar or nearly planar, with a significant bond shortening of about 8–10% relative to the corresponding single bond. Studies of the reactivity of these species confirm the presence of >Ge=X unsaturation as easy and nearly quantitative additions on the double bond are observed with many electrophiles and nucleophiles. Various types of cycloadditions ([2+1], [2+2], [2+3], [2+4]) are also possible with these species. The Ge=X derivatives appear extremely reactive, much more than the corresponding carbon analogues. Their reactivity as a germylene has never been observed (except in Lappert's digermene), but only their behavior as doubly bonded germanium, proving that they retain their structural integrity in solution.

Stable >Ge=X compounds are of particular interest because their reactivities can be thoroughly studied whereas studies of transient species are severely limited. The study of these new 'organometallic functions' is now in progress and appears very promising, particularly in organic and organometallic synthesis, including organometallic polymers. Although the chemistry of low-coordinated germanium species has developed rapidly during the last 10 years, many aspects remain to be examined, such as the synthesis and isolation of new types of doubly bonded germanium species including stable >Ge=B–, >Ge=Si<, >Ge=Sn<, >Ge=As– and >Ge=O. Another challenge is the preparation of triply-bonded germanium species –Ge≡X, germa-allenic derivatives X=Ge=X, heterogermadienes and heterodigermadienes (for example: >Ge=X–X=X, $X{=}\overset{|}{\mathrm{Ge}}{-}X{=}X$, >Ge=X–X=Ge<, $X{=}\overset{|}{\mathrm{Ge}}{-}\overset{|}{\mathrm{Ge}}{=}X$… with X = C, N, P) which, as yet, have neither been isolated nor clearly characterized by a trapping reaction.

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