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Phosphasila-, phosphagerma-, and phosphaarsaallenes —P=C=E (E = Si, Ge, As) and arsa- and diarsaallenes —As=C=E´ (E´ = C, As)*

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The paper reviews the contribution from our group to the studies of heteroallenes. The transient 1,3-phosphasilaallene ArP=C=Si(Ph)Tip (Ar = 2,4,6-tri-*tert*-butylphenyl, Tip = 2,4,6-triisopropylphenyl) and 1,3-phosphagermaallene $ArP=C=GeMes_2$ (Mes = 2,4,6-trimethylphenyl) were characterized below −40 °C by NMR spectroscopy and chemical trapping. These compounds dimerize above −40 °C through two routes. With increased steric hindrance on germanium, the phosphagermaallene $ArP=C=Ge(Bu^t)Tip$ was stabilized as monomer at room temperature. 3-Chloro-2-lithio-1,3-phosphasilapropene $ArP=C(Li)Si(Cl)CMeR_2$ ($CMeR_2$ = 9-methylfluorenyl) behaves, at least in some cases, as a synthetic equivalent of the functionalizable allene $ArP=C=Si(Cl)CMeR_2$. Arsaallene $ArAs=C=CR_2$, phosphaarsaallenes ArP=C=AsAr and ArP=C=AsDmt (Dmt = 2,6-dimesityl-4-methylphenyl), and diarsaallene ArAs=C=AsAr exhibit a higher thermal, air, and moisture stability than the above phosphasilaallenes and phosphagermaallenes. The physicochemical data for the arsaallenes and diarsaallenes, particularly, their X-ray structural parameters, display a bonding system close to allenes. On going down the Periodic table, the stabilization becomes more difficult. For this reason, tin allenic derivatives are very rare and antimony allenic compounds have not yet been isolated.

Key words: phosphasilaallenes, phosphagermaallenes, phosphastannaallene, arsaallene, phosphaarsaallenes, diarsaallene, phosphaalkenes, arsaalkenes.

Introduction

Alkenes, carbonyl derivatives, and imines are known for more than one century and are very important compounds in organic chemistry. However, it was not the case for their heavier analogs in which one or two elements of the second row (C, N) are replaced by heavier elements (Si, Ge, P, As, ...). The lack of studies in this field was partly due to the double bond rule,[1] considered as valid until the 1970s, stating that stable (p—p)π-multiple bonds could not be formed between elements of the third or fourth rows.

After the synthesis in 1981 of a series of stable diphosphene ArP=PAr (Ar = 2,4,6-tri-*tert*-butylphenyl),[2] silene $(Me_3Si)_2Si=C(OSiMe_3)Ad$ [3] (1-adamantyl), and disilene $Mes_2Si=SiMes_2$ (Mes = 2,4,6-trimethylphenyl),[4] this field attracted a widespread interest. This is due to their unusual structures (for example new bonding models have to be imagined), physical and chemical properties (generally high reactivity of the double bond allowing them to be used as building blocks in organometallic chemistry).

Now, almost all the $E^{14}=E^{14}$, $E^{14}=E^{15}$, and $E^{15}=E^{15}$ combinations (E^{14} = C, Si, Ge, Sn; E^{15} = N, P, As) have been characterized and in most cases isolated. Our group has been involved in the synthesis of the first stable or NMR-evidenced sample of some of these new organometallic functions, such as phosphagermene —P=Ge<,[5] phosphastannene —P=Sn<,[6] germene >Ge=C<,[7] stannene >Sn=C<,[8] germastannene >Ge=Sn<,[9] phosphaarsene —P=As<,[10] and diarsene —As=As—.[11]

These doubly bonded derivatives are generally stabilized owing to large steric hindrance, which prevents their dimerization or oligomerization. Complexation by transition metals is also used, whereas electronic effects, even if they are sometimes important, generally do not play a crucial role in the stabilization of the monomeric species.

For reviews on M=C compounds, see: M = Si,[12] M = Ge,[12e,12g,12j,13] M = Sn,[12e,12g,12j,13d,13e] M = P,[12g,14] and M = As.[15]

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After the study of compounds with one double bond, a new and exciting challenge was the preparation and characterization of heavy analogs of another important organic function such as the allene function. Such derivatives with at least one carbon atom replaced by a heavier Group 14 or 15 element, are referred to as heteroallenes. Great progress has been made for the last 10 years in the study of these compounds with two adjacent double bonds in many groups. For reviews on heteroallenes M=C=X, see Refs. 14g and 16.

This paper is a review on the contribution from our group of the University Paul Sabatier of Toulouse to the study of heteroallenes.

We were interested in two types of heteroallenes:

— those with two heavy elements of Groups 14 and 15 (P), such as —P=C=E_{14}< (E_{14} = Si, Ge, Sn),

— those with one or two heavy elements of Group 15, such as arsenic and antimony.

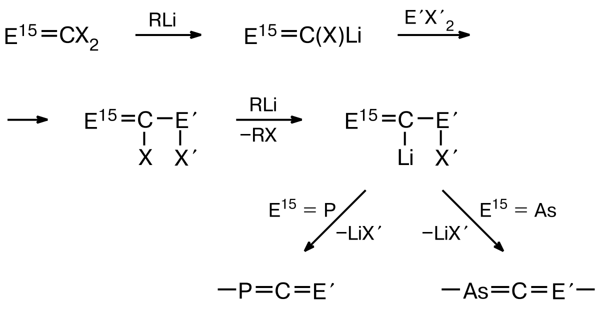
Thus, we will describe transient 1,3-phosphasilaallene and 1,3-phosphagermaallene —P=C=M< (M = Si, Ge), attempted syntheses of a 1,3-phosphastannaallene —P=C=Sn<, stable 1,3-phosphagermaallene —P=C=Ge<, 3-chloro-2-lithio-1,3-phosphasilapropene —P=C(Li)=Si(Cl)<, 1-arsaallene —As=C=C<, 1,3-phosphaarsaallenes —P=C=As—, 1,3-diarsaallene —As=C=As—, and, finally, attempted synthesis of an allenic derivative of antimony.

These new families of heteroallenes were unknown at the beginning of our work.

General approach to heteroallenes

As the simultaneous creation of two double bonds appeared unlikely, we chose to first create the P=C or As=C double bond, which is generally both thermodynamically more stable and less reactive than the Si=C [12] or Ge=C [12e,12g,12j,13] double bond. The dichloro- or dibromophosphaalkenes $ArP=CX_2$ [17] (X = Cl, Br) were used as building blocks (Scheme 1). The carbenoids ArP=CX(Li)[18] possess different thermal stability depending on their stereochemistry (*Z* or *E*) and on the halogen on carbon: the bromo carbenoid (X = Br) and the *E*-chloro carbenoid (X = Cl) decompose around −80 °C to give after rearrangement phosphaalkyne ArC≡P, whereas the *Z*-chloro carbenoid is stable up to room temperature.[18b] Thus, depending on the coupling reagent, the chloro- or bromo- compounds were chosen as starting materials. In the arsenic series, the corresponding dihaloarsaalkenes were employed.[19] The general reaction route to the heteroallenes was the following (Scheme 1).

Scheme 1



X, X′ = F, Cl, Br; E′ = Si, Ge, As

In most cases, we attached to phosphorus atom the bulky 2,4,6-tri-*tert*-butylphenyl group that is well known to stabilize doubly bonded phosphorus compounds.[12g,14]

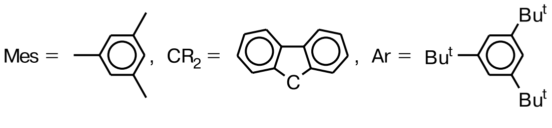
Compounds $P=C=E^{14}$ (E^{14} = Si, Ge)

Transient phosphasila- and phosphagermaallenes

Synthesis of a phosphagermaallene. The first allenic compounds with two heavy elements of Groups 14 and 15 to be chemically and physicochemically characterized were transient phosphasilaallenes —P=C=Si< and phosphagermaallenes —P=C=Ge< prepared by the general process previously described.

In the case of phosphagermaallenes,[20] the best results for the creation of the Ge=C unsaturation were obtained with fluorine on germanium; the use of fluorine instead of chlorine prevents alkylation at germanium and reduction of the Ge—Cl function by the lithium compound: note that most of the germenes >Ge=C< have been obtained by a dehydrofluorination of their >Ge(F)—C(H)< precursors.[7,21] The mesityl group at the Ge atom exhibits good stabilizing properties in doubly bonded germanium compounds, such as germene **1a**,[7] phosphagermene **1b**,[5] or germanimines **1c**.[22]

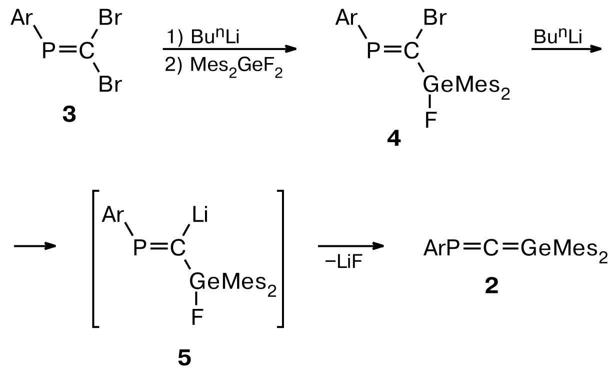
$Mes_2Ge=CR_2$ **1a** $Mes_2Ge=PAr$ **1b** $Mes_2Ge=NR$ **1c**



R is substituted thiophene or aryl groups

The dehalogenation route was comparable to the method used by Wiberg for the formation of transient germenes.[23] Phosphagermaallene **2** was thus prepared[20] in 65—70% yield (according to ^{31}P NMR spectroscopy) by metallation of dibromophosphaalkene **3** followed by coupling with Mes_2GeF_2 to form compound **4**, which in turn was treated with BuLi to give compound **5** (Scheme 2).

Scheme 2

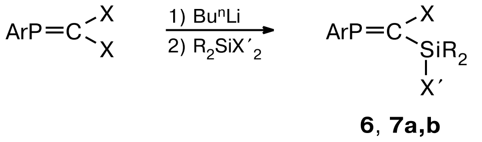


Compound **2** could not be isolated because of its thermal instability, but it was unambiguously characterized by its NMR data at –40 °C (see further).

Synthesis of phosphasilaallene. As phosphagermaallene **2** dimerized above –40 °C, we supposed that the same event could occur with its silicon analog. In order to have a further insight into the nature of the mechanism (concerted or multistep biradical that is still controversial) of a possible dimerization, we substituted the silicon atom by two different groups.

Attempts to prepare dihalophosphasilapropene $Mes_2Si(X)C(X')=PAr$ (X, X′ = Cl, Br) failed.[24] This is a great difference with the case of its germyl analog with the same Mes groups on germanium. This is probably due to the shorter Si—C than Ge—C bond length that increases the steric hindrance and prevents the coupling reaction between the phosphorus and silicon moieties. Thus, the steric hindrance on silicon was slightly lowered with a phenyl and a 2,4,6-triisopropylphenyl (Tip)[25] or even two phenyl groups[24] (Scheme 3).

Scheme 3

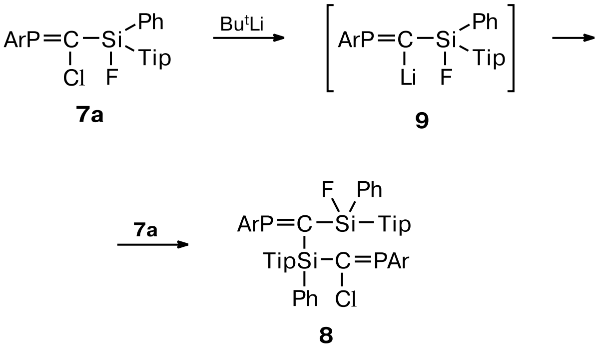


6: X = Br, X′ = F, $R_2 = Ph_2$;[24]
7a: X = Cl, X′ = F, R_2 = Tip, Ph;[25]
7b: X = X′ = F, R_2 = Tip, Ph [25]

The debromofluorination of compound **6** by *tert*-butyllithium at low temperature afforded a complex mixture of compounds giving ^{31}P NMR signals between 297 and 468 ppm indicative of an $\lambda^3\sigma^2$-P structure.[24] We suppose that, due to not a large enough steric hindrance, many reactions occurred involving or not the preliminary formation of phosphasilaallene followed by its dimerization, addition of lithium compounds to the Si=C unsaturation, or direct alkylation of silicon. This experiment demonstrated a great role of the steric hindrance in such types of derivatives.

When carbon was substituted by a chlorine atom and silicon by a fluorine atom, an unexpected reaction occurred leading to **8** (Scheme 4).[26] This reaction probably involved preliminary Li/Cl exchange in **7a** to form **9** followed by condensation with **7a**.

Scheme 4



This difference in reactivity with the case of germanium is probably due, among other factors, to the strong Si—F bond. Compound **8** was obtained in the form of diastereoisomers **8a** and **8b**,[26] whose ^{31}P NMR spectral parameters are presented below.

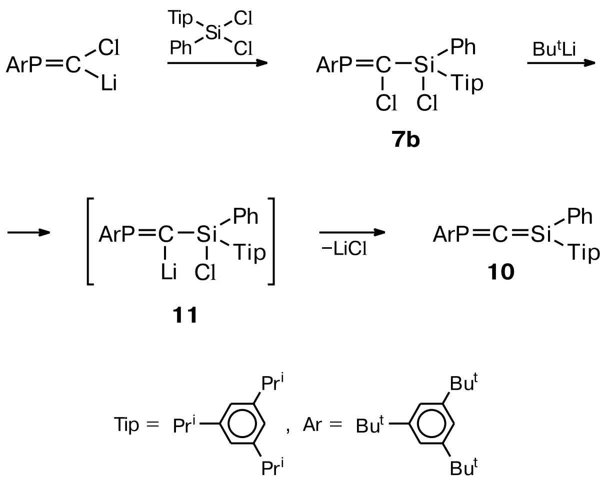
Compound	δ	$^3J_{P,F}$	$^4J_{P,P}$
		Hz	
8a	332.1, 466.2	10.5	17.8
8b	327.3, 463.0	8.0	17.8

By contrast, with chlorine at the silicon atom, the formation in 60% yield (according to NMR study) of the transient phosphasilaallene **10** was observed[25] at low temperature (Scheme 5).

When the reactions of formation of the phosphasila- and phosphagermaallenes were monitored by NMR techniques between –85 °C and room temperature, the intermediate formation of lithio derivatives **5** and **11** was proved by ^{31}P NMR by signals at very low field (397.4 ppm, $J_{P,F}$ = 16.9 Hz (**5**); 417.6 ppm (**11**)).

Physicochemical studies. Phosphasila- and phosphagermaallenes **10** and **2** were evidenced at –40 °C by NMR spectroscopy, mainly for ^{13}C nucleus, where characteristic very low-field shifts were found. Similar low-field shifts were observed in the ^{29}Si NMR and ^{31}P NMR spectra (Table 1). They are comparable to those observed in silaallenes >Si=C=C< and germaallenes >Ge=C=C<. The signal at low field in ^{31}P NMR is indicative of a P=C unsaturation with the carbon bonded to an electropositive element.

Scheme 5



In the silaallene $(Pr^i_3Si)_2Si{=}C{=}C(SiMe_3)_2$ recently prepared by Sekiguchi,[33] due to the presence of electropositive silicon both on Si and terminal C, very different chemical shifts were observed for ^{13}C NMR (268.3 ppm) and particularly for the ^{29}Si NMR spectra (–64.5 ppm, which is the most upfield shifted signal for a Si=C species). These assignments were confirmed by calculations for the model compound $(H_3Si)_2Si{=}C{=}C(SiH_3)_2$, whose results (292.6 and –50.8 ppm, respectively) were found to be in good agreement with the experimental values. With alkyl or aryl groups, the ^{29}Si NMR signals are in the range of 44—59 ppm, except for two cases (13.1 ppm[27e] and 16.2 ppm[27f]).

The ^{31}P NMR values of phosphaallenic derivatives are extremely dependent on the nature of the X atom: the more electronegative the X atom is, the more high-field shifted the ^{31}P NMR signal.

Dimerization. Phosphasila- (**10**) and phosphagermaallenes (**2**) are stable in solution below –40 °C but on warming to room temperature, two types of dimerization occurred[20,25]:

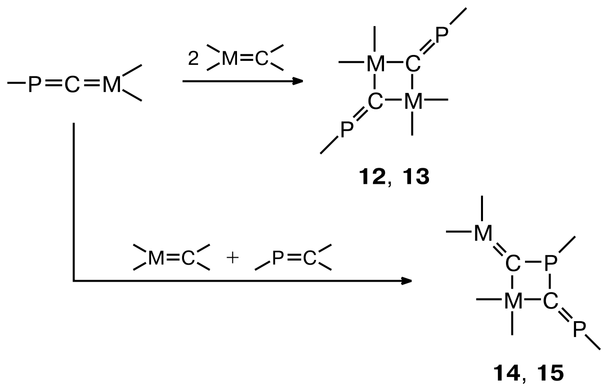
— expected head-to-tail dimerization *via* two M=C double bonds (M = Si, Ge) to give 1,3-dimetallacyclobutanes **12** and **13**,

— unexpected dimerization by one M=C and one P=C double bond, leading to the unsymmetrical dimers **14** and **15** (Scheme 6).

Table 1. ^{13}C, ^{29}Si, and ^{31}P NMR spectroscopic data for heteroallenes

Compound	δ (*J*/Hz)			References
	^{13}C	^{29}Si	^{31}P	
ArP=C=Si(Tip)Ph	269 ($J_{C,P}$ = 45.8)	75 ($J_{P,Si}$ = 18)	288	25
ArP=C=GeMes$_2$	280 ($J_{C,P}$ = 54.3)	—	239	20
>Si=C=C<	216—228	44—59	—	27
>Ge=C=C<	235—243	—	—	28
—P=C=C<	209—250	—	39—92	29
—P=C=N—	209—250	—	–64—–135	30
—P=C=P—	209—250	—	140—169	29a, 31
—P=C=O	209—250	—	–180—–207	32

Scheme 6



M = Si (**12**, **14**), Ge (**13**, **15**)
Ratio **12** : **14** = 40 : 60,[25] **13** : **15** = 12 : 88.[20]

Head-to-tail dimers **12** and **13** were characterized by very low-field shifts in ^{31}P NMR spectra (431.9 and 425.4 ppm (**12**),[25] 381.0 and 374.7 ppm (**13**)[20]), rather characteristic of the presence of two electropositive elements at the carbon doubly bonded to phosphorus.[14a]

The structure of dimer **12″** was determined by X-ray diffraction and showed a nearly planar Si_2C_2 four-membered ring with a small fold angle (4.7° and 5°) along the Si—Si and C—C axes.[25]

A thermodynamic equilibrium was observed between isomers **12′**/**12″** and **13′**/**13″**. Isomers **12′**/**13′** were initially formed giving finally the major ones **12″**/**13″** with two Ar group in *cis*-orientation toward the P=C...C=P axis (Scheme 7).[20,25]

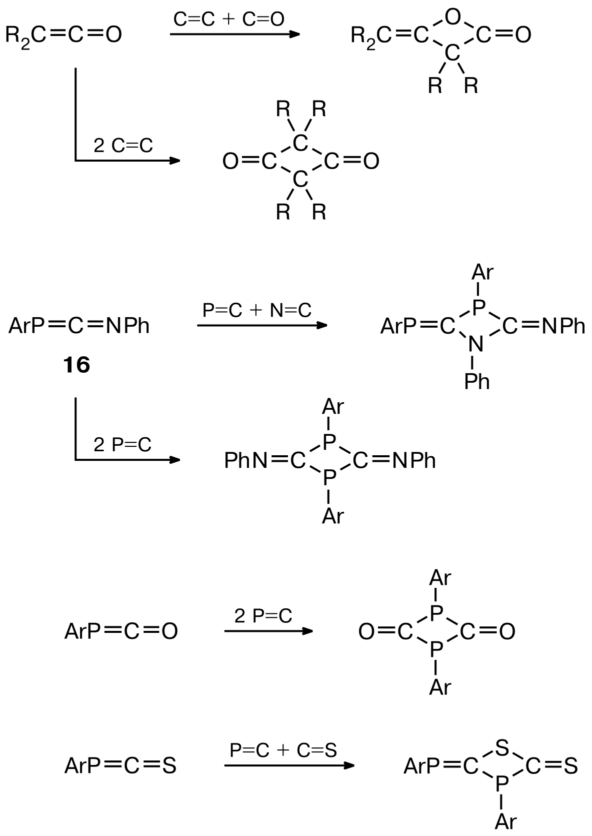
Scheme 7

M = Si (**12**), Ge (**13**)

Unsymmetrical dimers **14**/**15** are characterized by AX systems in ^{31}P NMR spectra with the expected low-field shifts for the dicoordinate phosphorus atoms and a higher field shift for the tricoordinate ones with large ${}^2J_{P,P}$ coupling constants. Compound **14**: 40.5 (d), 305 (d), J = 254.0 Hz[25]; compound **15**: 61.3 (d), 269.5 (d), J = 225.4 Hz.[20]

These two types of dimerization (Scheme 8) have previously been observed in other heteroallenes such as ArP=C=O,[32b] R_2C=C=O,[34] ArP=C=NPh,[35] and ArP=C=S.[36]

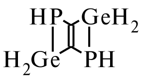
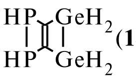
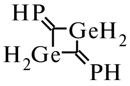
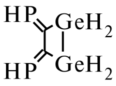
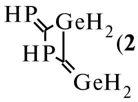
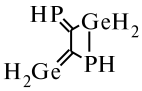
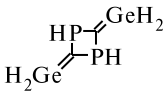
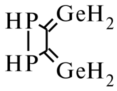
Scheme 8



Thus, phosphasila- (**10**) or phosphagermaallene (**2**) exhibit a behavior close to that of azaphosphaallenes **16** in their dimerization.

Restricted Hartree—Fock calculations were performed with the GAUSSIAN-92 package on the model compound HP=C=GeH_2.[20] The most stable dimers appeared to be the bicyclic compounds presenting "butterfly" structures **17** and **18** (see Table 2) formed by two successive P=C or Ge=C cycloadditions. The formation of such derivatives should be possible owing to the differences between the C=C double bond length (1.34 Å) and the P—P, Ge—P, and Ge—Ge distances (respectively about 2.25, 2.40, and 2.50 Å), which relieve the cyclic strain that could at first sight be expected.

Table 2. Relative energies (E_{rel}/kcal mol^{-1}) for dimers of phosphagermaallene HP=C=GeH_2

Dimers	Reaction sites	E_{rel}
 (**17**),  (**18**)	2 Ge=C + 2 P=C	0
 (**19**),  (**20**)	2 Ge=C	15
 (**21**),  (**22**)	Ge=C + P=C	33
 (**23**),  (**24**)	2 P=C	58

The energy ordering of the possible dimers was found to be **17**/**18** < **19**/**20** (~15 kcal mol^{-1}) < **21**/**22** (~33 kcal mol^{-1}) < **23**/**24** (~58 kcal mol^{-1}). Dimers **20**, **22**, and **24** are more stable than the corresponding dimers **19**, **21**, and **23** (1, 6, and 5 kcal mol^{-1}, respectively) due to a butadiene-type conjugation. However, since the steric strain in **20**, **22**, and **24** is much more important than that in **19**, **21**, and **23**, the latter could be favored.

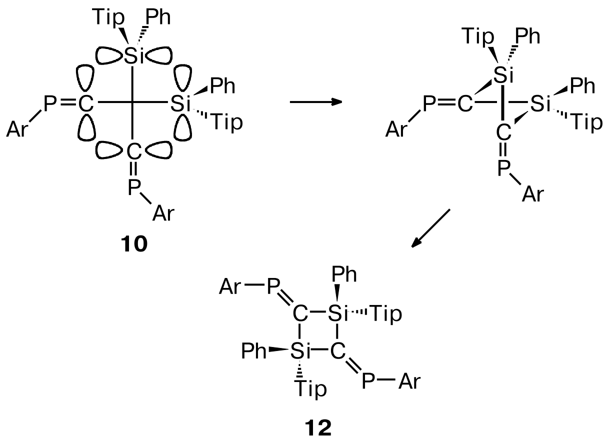
Due to a large size of the Mes and Ar groups, there are some differences between experiment and calculations based on the model compounds. No butterfly structures, analogous to **17** and **18**, were observed for steric reasons, and the only two characterized dimers were those corresponding to **19** and **21**.[20]

The mechanism of dimerization of **2** and **10** deserves some comments. Many theoretical[37] and experimental[38] studies have been performed in order to better know the mechanism of dimerization of silenes. A concerted [$2\pi_s+2\pi_s$] mechanism was postulated by Schaefer,[37a] whereas a stepwise mechanism with preliminary formation of a short-lived biradical intermediate was postulated by Bernardi.[37b]

In the case of silene **10**, a stereospecificity was observed, with the formation of the most crowded dimer **12** (Tip groups in the *cis*-position of the four-membered ring) whatever the solvent (ether, toluene) used. These results seem to be in agreement with a concerted mechanism. Although such the concerted supra-supra process is theoretically forbidden by the Woodward—Hoffmann rules, the polarization in the Si=C double bond in molecule **10** probably leads to a relaxation of these rules (Scheme 9).

However, the two-stage mechanism cannot be totally excluded since, due to the large size of Tip and Ar groups,

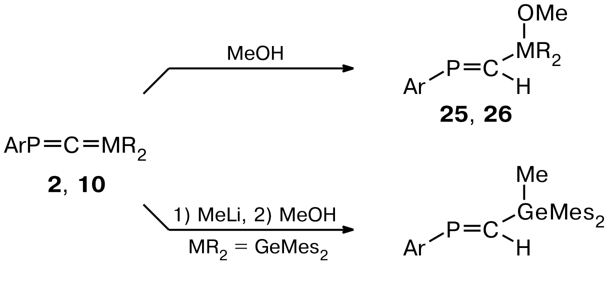
Scheme 9



only one type of approach should be favored also leading to the stereospecificity.[25]

Reactivity. The formation of allenic structures **2** and **10** was proved by chemical trapping of these heteroallenes at –40 °C with methanol and methyllithium (Scheme 10).[20,25]

Scheme 10



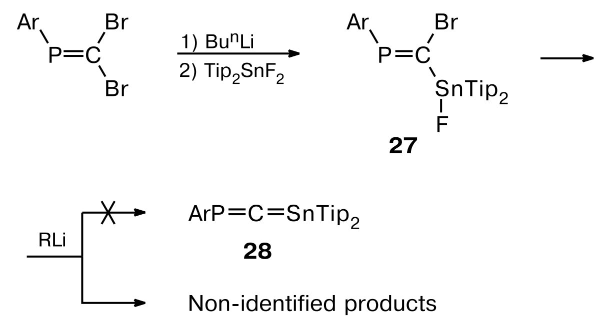
MR_2 = Si(Tip)Ph (**25**), $GeMes_2$ (**26**)

Addition of MeOH was chemoselective with exclusive addition to the M=C double bond (even with an excess, the P=C double bond was unreactive) according to the expected $M^{\delta+}=C^{\delta-}$ polarity. The sole *E*-isomer was obtained, as proved by the value of the $^2J_{P,H}$ coupling constants (23.5 Hz (**25**)[25] and 25.5 Hz (**26**)[20]). In the *Z*-isomers, the coupling should be around 18 Hz (for example, for *Z*- and *E*-ArP=C(H)$SiMe_3$ it is 18 and 24.7 Hz, respectively).[18a,c] The change in the *cis*-rule ($^2J_{P,H}$ coupling constant was expected to be greater for *Z*- than for *E*-isomer) has been discussed by Bickelhaupt[18a] who stated that the low electronegativity of silicon or germanium attached to the carbon atom plays a great role.

Attempted synthesis of phosphastannaallene

The stabilization is of course more and more difficult on going down the Periodic table. Thus, although many silenes >Si=C< are known,[12] much less germenes >Ge=C< have been prepared,[12e,g,j,13] and very few stannenes >Sn=C< have been isolated or even physicochemically characterized.[12e,g,j,13d,e] Due to the presence of two double bonds, the stabilization of phosphastannaallene –P=C=Sn< should be more difficult and represents a great challenge. Because of the large size of tin atom, bulkier groups than Mes (used on germanium in the phosphagermaallene) are necessary, such as two 2,4,6-triisopropylphenyls. By the procedure previously described for silicon and germanium compounds, fluorophosphastannapropene **27** was prepared (Scheme 11).[24]

Scheme 11



R = Bu^n, Bu^t

$\delta_{^{31}P} = 321.6$, $\delta_{^{119}Sn} = -103.0$,
$J_{P,Sn} = 505$ Hz, $J_{F,Sn} = 2458$ Hz.

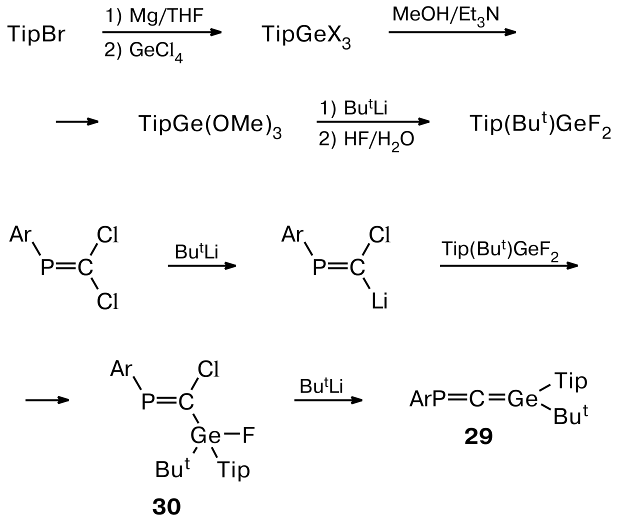
Attempts to prepare phosphastannaallene **28** by debromofluorination of **27** with Bu^nLi or Bu^tLi in various solvents (THF, toluene, *etc.*) were until now unsuccessful;[24] many signals between 298 and 442 ppm were detected in ^{31}P NMR spectroscopy. The transient formation of the expected phosphastannaallene could neither be evidenced nor ruled out.

Attempts to prepare —P=C=Sn< compounds are now under investigation with bulkier groups, both on tin and phosphorus, such as 2,6-dimesityl-4-methylphenyl.

Stable phosphagermaallene 29

Synthesis. In order to prepare an isolable phosphagermaallene, more convenient for studying the chemical behavior than a transient one, bulkier groups on germanium were used. However, whereas the coupling between Mes_2GeF_2 and ArP=C(Br)Li occurred in very good yield,[20] the latter failed to react with Tip_2GeF_2 because of a too large steric hindrance of the Tip groups on germanium.[24] This reaction illustrates the difficulty in the chemistry of doubly bonded main group elements to find the right group, potentially able to stabilize the low-coordinate species but not too large in order not to prevent the formation of their precursors. Thus, an intermediate steric hindrance on germanium with a Tip and a Bu^t groups was chosen (Scheme 12).

Scheme 12



$X_3 = Cl_3, Cl_2Br, ClBr_2, Br_3$

Phosphagermapropene **30** was prepared from $TipGeX_3$.[39] Like precursors **4** and **7b** of transient phosphasila- and phosphagermaallene, derivative **30** was obtained as a unique probably the *Z*-stereoisomer (such a stereochemistry was proved in the arsenic series; see below). This isomer is formed through the most probable mechanism, involving Hal—Li exchange from the least hindered side containing the *E*-chlorine, giving a carbenoid with the lithium atom in the *anti*-position with respect to the Ar group. This stereochemistry has previously been postulated.[18]

Addition of *tert*-butyllithium to a solution of **30** at −80 °C followed by warming to room temperature afforded nearly quantitatively the expected phosphagermaallene **29** (see Scheme 12).[39] Orange solutions of **29** are extremely air- and moisture-sensitive but can be kept without changes at room temperature for one week in inert atmosphere.

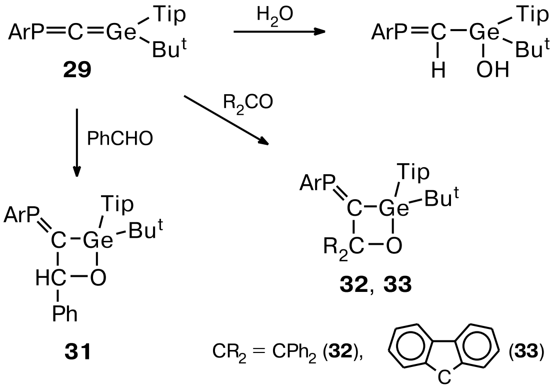
This is the first stable allenic compound with two heavy Group 14 and 15 elements. In comparison with transient phosphagermaallene $ArP{=}C{=}GeMes_2$, the higher stability of **29** is due to a better steric protection by Tip and Bu^t groups at the germanium atom instead of two Mes groups. Thus, a slight change in the steric hindrance dramatically changes the behavior of such species.

Physicochemical and chemical studies. Compound **29** was unambiguously characterized by its low-field shifts in ^{13}C and ^{31}P NMR (280.4 and 249.9 ppm, respectively, $J_{P,C}$ = 62.1 Hz) close to those found for transient compound **2**, and by its chemical reactivity.

Water adds regiospecifically to the Ge=C unsaturation. The [2+2] cycloadditions were observed with the C=O moiety of aldehyde (benzaldehyde) and ketones (benzophenone, fluorenone), leading to air- and moisture-stable four-membered ring compounds **31—33** with an exocyclic P=C double bond.[39] As expected, the oxygen atom is linked to germanium. These oxagermetanes were characterized with ^{13}C NMR spectra by a doublet (coupling with phosphorus) for the carbon bonded to oxygen. In the case of compound **31** prepared from benzaldehyde, two diastereoisomers were obtained in a ratio of 65 : 35 due to the assimmetric Ge and C(O) atoms.

An X-ray structure determination for heterocycle **33** prepared with fluorenone showed slightly elongated bonds in the four-membered ring and the formation of the *Z*-isomer. Although it is the most hindered structure (Ar and Ge(Bu^t)Tip in the *cis*-position), its formation can be explained by the preferential addition of fluorenone to the less hindered side of the Ge=C bond, *i.e.*, in the *cis*-position to the lone pair of phosphorus (Scheme 13).[39]

Scheme 13



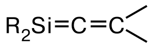
Allene **29** also reacts with sulfur, *tert*-butyllithium, and α-ethylenic aldehydes and undergoes thermolysis. These reactions are now under investigation.

Bonding structure. Some theoretical studies[40] have been performed for the —P=C=X compounds (X = C, N, P), which predicted a P—C—X bond angle generally comprised between 172 and 178° close to the structures found by X-ray studies. In the case of >M=C=C< derivatives (M = Si, Ge), the 1-metallaallene framework was predicted by Trinquier and Malrieu[41] to be nonlinear with *trans*-bending of the substituents. Their calculations were based on the determination of the difference between the sum of the singlet-triplet energy separations for the two fragments >M: and :C=C< ($\Sigma\Delta E_{S-T}$) and the half sum of the energy of σ- and π-bonds ($E_{\sigma+\pi}$). Allenes >C=C=C< fulfil the inequality $0.5E_{\sigma+\pi} > \Sigma\Delta E_{S-T}$ and exhibit linearity. In heteroallenes, since silylenes or germylenes are singlets in the fundamental state, the inverse correlation is true ($0.5E_{\sigma+\pi} < \Sigma\Delta E_{S-T}$), which satisfies the condition for a bent structure.

A recent paper by Apeloig[42] reports that in >M=C=C< (M = Si, Ge, Sn, Pb) the deviation of the skeleton from linearity, the degree of pyramidalization at M, and the planarization energies for M increase in the series Si < Ge < Sn < Pb.

We failed to prepare the single crystals of **29** and, hence, an X-ray structure determination could not be performed. Hence, it was impossible to exactly determine the bonding situation in this compound (linear or not, *trans*-bent or not) and to compare our experimental results with calculations.

The transient or stable phosphasila- and phosphagermaallenes **2**, **10**, and **29** react mainly by the M=C double bond, and exceptionally by the P=C double bond in the sole dimerization. In all cases, the M—C—P skeleton remains stable and we never observed its cleavage. Consequently, a reactivity of silylene or germylene never occurred. In the silicon series, the chemical behavior of **10** is close to that of **34**; both compounds react as silaallenic derivatives. By contrast, "azasilaallenes" **35** [43—45] have a completely different chemical behavior: for example, addition of MeOH,[43] Et_3SiH,[43] 2,3-dimethylbutadiene,[43] or BH_3 [44] leads to isocyanide :C=N— and to the products of trapping of silylene R_2Si.



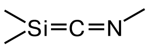
34

$R_2Si=C=N—$

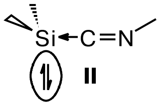
35

Moreover, the ^{29}Si NMR high-field chemical shifts for the >Si=C=N— compounds (–48 to –58 ppm)[43] are very different from those for silaallenes **34** (generally 44 to 58 ppm) and phosphasilaallene **10** (75.7 ppm).

Thus, it seems that the bonding structure of phosphasilaallene **10** (and also phosphagermaallenes **2** and **29**) is close to that of silaallenes **34**, and these compounds can be considered as heteroallenes. However, their structures are very different from that of derivative **35**, which is better represented as silylene—isocyanide adduct **II** rather than "azasilaallene" **I**.



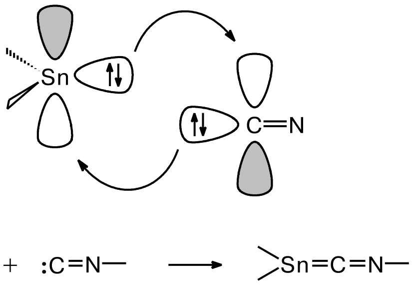
I



II

The same bonding situation is expected from calculations in silaketenes >Si=C=O with structures better described as complexes between silylenes and a CO moiety[46] and applies also to "azastannaallene" $R_2Sn=C=NMes$ (R = 2,4,6-$(CF_3)_3C_6H_2$) prepared by Grützmacher (Scheme 14).[47] The physicochemical data are in favor of a double π-donor-acceptor interaction similar to that reported for other tin unsaturated compounds, such as distannene $R_2Sn=SnR_2$ (R = $(Me_3Si)_2CH$).[48]

Scheme 14

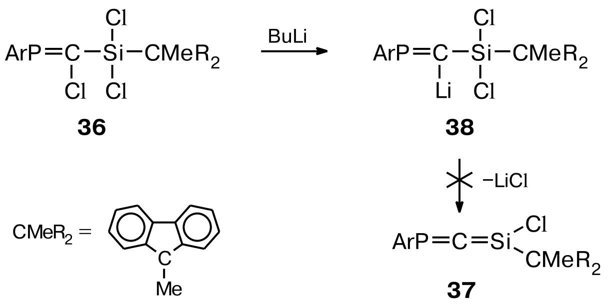


Chlorolithiophosphasilapropene

Stable doubly bonded compounds of silicon, germanium, phosphorus, and arsenic are generally substituted on the metal by bulky aryl or alkyl groups.[12—15] In order to potentially functionalize such low-coordinate species, we attempted to synthesize a phosphasilaallene with a chlorine atom on the silicon atom.

Thus we prepared phosphasilapropene **36** with two chlorine atoms and a fluorenylmethyl group (allowing generally easy crystallization) on silicon. However, the addition of butyllithium afforded stable (chloro)lithio derivative **38** instead of the expected phosphasilaallene **37** (Scheme 15).

Scheme 15



The structure of compound **38** was unambiguously proved by its chemical reaction with MeI and PhCHO giving with the latter an oxasiletane: such a four-membered ring compound should be expected in the reaction of phosphasilaallene $ArP=C=Si(Cl)CMeR_2$ with PhCHO. Thus, it seems that compound **38** similarly to phosphagermaallene (see above) could behave, at least in some cases, as a synthetic equivalent of phosphasilaallene **37**.

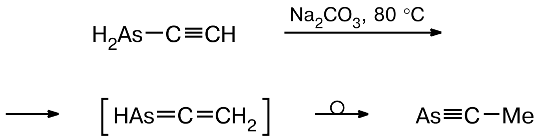
Preliminary theoretical calculations showed that compound **38** should be stabilized by π-interaction of the lithium atom with the Ar and Cp rings. The non-elimination of LiCl could also be due to a strong electrophilic character of the silicon atom substituted by a chlorine. This work is now in progress.

Compounds E^{15}=C=X (E^{15} = P, As, Sb; X = C, E^{15})

Many phosphaallenes —P=C=X (X = C, N, P) have been prepared by various groups.[14g,16a,29–31,35,49] Like all the heavy Main Group doubly bonded derivatives, these compounds are generally stabilized by bulky substitutents at phosphorus: the most commonly used are substituted phenyl ligands, mainly 2,4,6-tri-*tert*-butylphenyl. These phosphaallenes are more stable than the phosphasila- or phosphagermaallenes, whose Si(or Ge)=C double bond is extremely reactive toward unsaturated species or air and moisture. Some derivatives involving an arsenic double bond, the arsaalkenes —As=C<, have been reported in the literature[15,50–53] but stable allenic derivatives —As=C=X (X = C, N, P, O, S, *etc.*) were still unknown before we started our research.

The only allenic compound of arsenic reported in the literature has been postulated as an intermediate in the reaction of alkynylarsine with Na_2CO_3 leading to a transient arsyne, but no evidence was obtained by trapping or by physiochemical methods (Scheme 16).[54]

Scheme 16



It was interesting to prepare allenic compounds of arsenic to compare the physicochemical data, chemical behavior, and stability of the —As=C=X derivatives (X = C, P, As) with those of the phosphorus analogs.

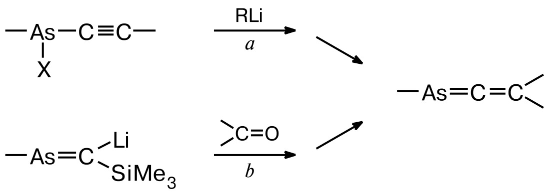
Since the As—C and As=C bonds are longer than the corresponding bonds with phosphorus atom, the same or even a larger steric hindrance are necessary to stabilize the allenic structures of arsenic compounds. Therefore, the 2,4,6-tri-*tert*-butylphenyl group or a bulkier group were generally used.

Arsaallene —As=C=C<

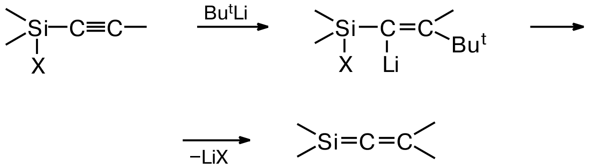
Synthesis. By comparison with the synthesis of phosphaallenes —P=C=C<,[14g,16a] various methods could be proposed. However, those involving the —As(H)Cl, —As=C=C=C<, or —As=C=O groups commonly used in the phosphorus analogs seemed to be difficult since these compounds should be first prepared. The most adequate methods for the preparation of arsaallenes seem to be procedures *a* and *b* (Scheme 17).

A route similar to method *a* involving the addition of Bu^tLi to ethynylhalosilanes followed by elimination of lithium halide was successful for silaallene >Si=C=C< (Scheme 18).[27d,e]

Scheme 17

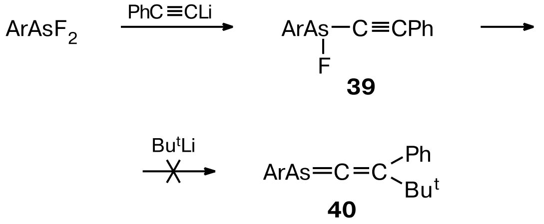


Scheme 18



However, route *a* involving ethynylfluoroarsane **39** [55] failed to give the expected arsaallene **40** but resulted in a mixture of products of the cleavage of the As—Ar bond and the alkylation of arsenic (Scheme 19).

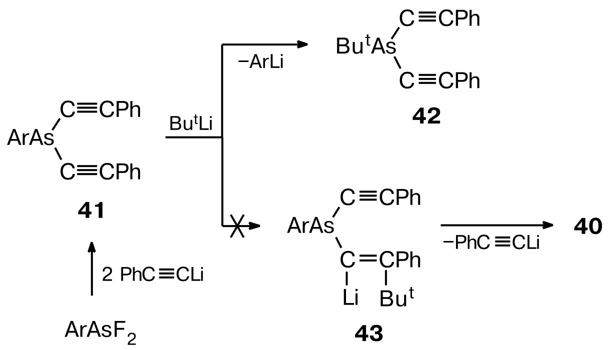
Scheme 19



Owing to the good leaving group property of the phenylethynyl substituent, the phosphaallene ArP=C=C(Mes)(Bu^t) was obtained by the addition of Bu^tLi to bis(ethynylphenyl)phosphine.[14g,56]

In sharp contrast, arsaallene **40** could not be prepared by such a route. The reaction of Bu^tLi with bis(ethynylphenyl)arsane **41** afforded exclusively diacetylenic com-

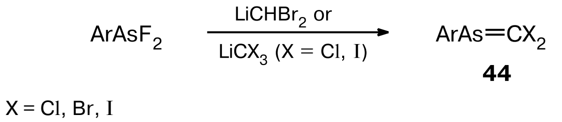
Scheme 20



pound **42** instead of **43** and **40**:[55] Bu^{t}Li does not add to the C≡C triple bond but cleaves the As—C(Ar) bond, being more labile than the P—C(Ar) bond, which was not cleaved in the phosphorus series (Scheme 20).

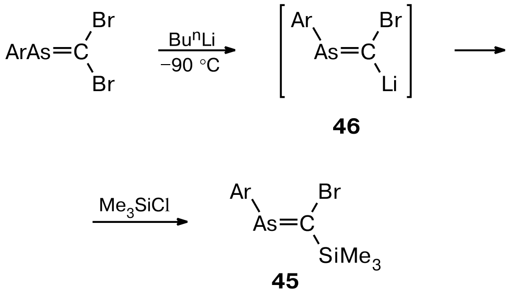
Route *b* involves the preliminary formation of dihaloarsaalkene ArAs=CX$_2$, which was prepared from ArAsF$_2$ by the following process (Scheme 21).[19]

Scheme 21



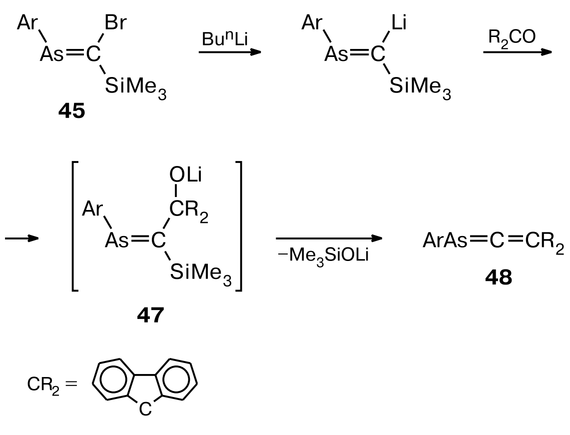
Arsaalkenes **44** are thermally stable and can be handled in air, at least for a short time. They can easily be functionalized at low temperature by X/Li exchange.[53] For example, arsaalkene **45** has been synthesized and characterized by X-ray diffraction, which proved the formation of the *Z*-isomer, through the nearly exclusive Br/Li exchange in *E*-bromide giving intermediate **46** like in its phosphorus analogs (Scheme 22).

Scheme 22



Successive addition of butyllithium and fluorenone to **45** leads to transient intermediate **47** that immediately loses Me$_3$SiOLi to give the expected arsaallene **48** (Scheme 23).[53]

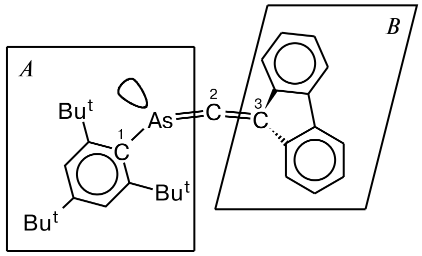
Scheme 23



Compound **48** is thermally stable and no formation of dimers was observed.

Physicochemical studies. The structure of **48** was evidenced by an extremely low-field shift in the ^{13}C NMR spectrum for the sp-hybridized C atom, comparable to that observed in phosphasila- and phosphagermaallenes and in the corresponding phosphaallene.[29p]

The structure of **48** was unambiguously proved by X-ray structural analysis.



The main features of this structure are the As—C(2)—C(3) bond angle of 169.7(2)° rather close to an ideal angle of 180°, and an angle between the planes *A* and *B* of 79.3°, which is in good agreement with the allene-like bonding system.

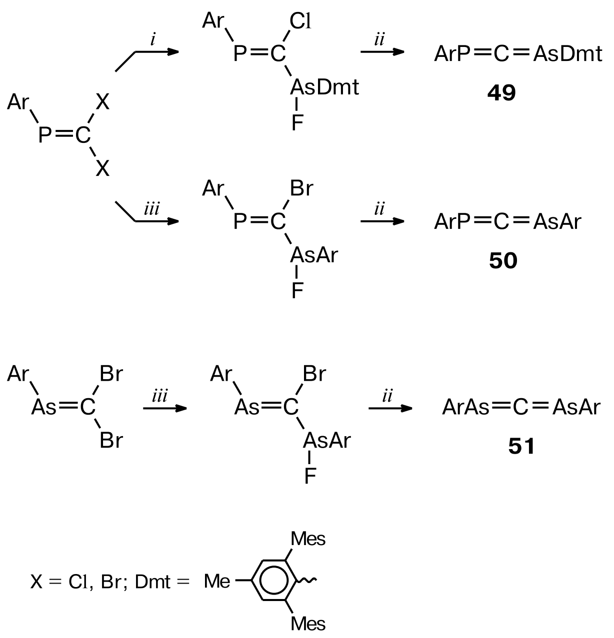
Molecule **48** possesses a very short As=C bond (1.754(2) Å). The shortening, in comparison to the As=C bond length in its precursor **45** (0.035 Å), is partly due to the smaller bond radius of the sp-hybridized C atom. A shortening of about 11% is observed in relation to the standard As—C single bond length, which lies generally in a range of 1.97—2.00 Å.[15]

Phosphaarsaallenes —P=C=As— and diarsaallene —As=C=As—

Synthesis. Since the stability of the arsaallene substituted at arsenic by the Ar group is high and no noticeable difference was observed with its phosphorus analog, it seems that a steric hindrance close to that used for diphosphaallenes —P=C=P— could allow the stabilization of their arsenic or diarsenic analogues. Phosphaarsaallenes **49**[57] and **50**[55] and diarsaallene **51**[52] were prepared by the procedure similar to that used for the synthesis of phosphasila- and phosphagermaallenes with the dihalophospha- (or arsa)alkenes ArE=CX$_2$ (E = P, As) and ArAsF$_2$ or DmtAsF$_2$[55] as starting materials (Dmt is 2,6-dimesityl-4-methylphenyl) (Scheme 24).

These three heteroallenes are thermal-, air- and moisture-stable both in the solid state (diamond-shaped pale

Scheme 24



Reagents and conditions: *i.* 1) Bu^nLi, –90 °C, 2) $DmtAsF_2$; *ii.* Bu^nLi, –90 °C; *iii.* 1) Bu^nLi, –90 °C, 2) $ArAsF_2$.

yellow crystals) and in solution. They are soluble in all usual organic solvents.

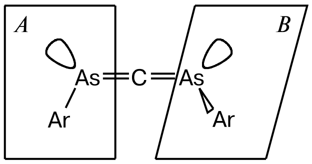
Physicochemical studies. Extremely low-field shifts, up to 300 ppm, were observed in ^{13}C NMR spectra (Table 3), which are characteristic of the expected allenic structure. ^{31}P NMR spectra displayed signals around 160 ppm, close to those found for diphosphaallenes in a range of 140—169 ppm.[14g,16a,29a,31]

The X-ray structure of diarsaallene **51** reminds, like in the case of arsaallene $ArAs=C=CR_2$, the allene bonding system: the angle between planes *A* and *B* is 77.6(6)°, the As—C—As bond angle is 175.6(6)°, and very short As=C bond length (1.7584(9) Å, being the shortest reported until now).

The ^1H NMR spectra of **50** and **51** at room temperature display very broad signals for *o*-methyl substituents on Ar groups. This is due to a slow rotation of the Ar groups (probably in a gear mode) caused by the severe steric hindrance. A dynamic NMR study between –60 °C and +60 °C allowed the determination of the rotation barriers in compounds **50** and **51**. As expected, its value in diarsaallene **51** (12.9 kcal mol^{-1})[52] is slightly lower than that in phosphaarsaallene **50** (13.6 kcal mol^{-1}),[57] because the P—C bond length is shorter than the As—C one causing a larger steric hindrance. A rather similar value was obtained for ArP=C=PAr.[58]

Table 3. Spectroscopic data for phosphaarsa- and diarsaallenes

Compound	NMR, δ (*J*/Hz)		UV, λ/nm (ε)	References
	^{31}P	^{13}C		
ArP=C=AsAr	159.7	299.5 (d, $J_{P=C}$ = 75.1)	274 (45634), 374 (1267)	57
ArP=C=AsDmt	166.9	300.7 (d, $J_{P=C}$ = 75.5)	—	55
ArAs=C=AsAr	—	296.5	282 (97674), 388 (838)	52



51

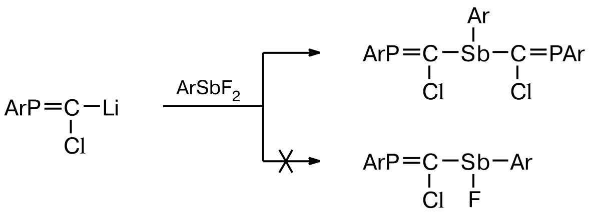
Allenic derivatives of antimony

Doubly bonded compounds of antimony are rare; these are several Sb=C, Sb=P, Sb=Sb, and Sb=Bi derivatives (see review[59]). In the case of the —Sb=C< compounds,[60] only few of them have been described or postulated.

Thus, the synthesis of stable stibaallenic derivatives —Sb=C=X (X = C, P) appears to be a great challenge which is now under active investigation.

The first attempts with the Ar or Dmt groups attached to antimony show that, due to a greater size of this metal compared to arsenic, disubstituted products are preponderant over monosubstituted ones (Scheme 25).

Scheme 25



Nevertheless, the monoadduct $ArP=C(SiMe_3)—Sb(F)Ar$ with the Ar group at antimony was prepared but the further reaction with butyllithium did not afford the expected phosphastibaallene ArP=C=SbAr.

Moreover, the (Ar)C—Sb bond is easily cleaved during recrystallization even at –20 °C and appears relatively weak, particularly in halogenated solvents (CH_2Cl_2, $CHCl_3$) or with traces of moisture.

Attempts are now made with other leaving groups at carbon and antimony and bulkier substituents.

Conclusion

Some remarks can be drawn from this work on allenic derivatives of silicon, germanium, phosphorus, arsenic, and antimony and from the literature.

— Stabilization of the E=C=E´ derivatives (E, E´ = C, Si, Ge, Sn, P, As, Sb) needs very bulky groups at the E and E´ atoms; a slight change in the steric hindrance of the substituents at E and E´ changes drastically the stability of the heteroallenes; it is particularly true for the phosphasila- and phosphagermaallenes —P=C=E< (E = Si, Ge). The choice of groups at E and E´ appears very difficult: when they are too bulky, no coupling of the E=C and E´ moieties occurs and when they are not bulky enough, the heteroallene dimerizes immediately.

— Si=C and Ge=C double bonds are extremely air- and moisture-sensitive, and —P=C=Si< or —P=C=Ge< compounds should be handled in inert atmosphere, in sharp contrast with the —P=C=P—, —P=C=As—, —As=C=As—, or —As=C=C< derivatives, which are air- and thermally stable.

— Derivatives of the type E^{14}=C=E^{14} with two heavy elements of Group 14 are still unknown. However, a recent paper by Apeloig[61] predicted that 1,3-disilaallenes could be obtained from disilacyclopropylidenes and their carbenoids.

— Fact that derivatives with two heavy elements of Group 15 E^{15}=C=E^{15} have been synthesized illustrates the difference between elements of Groups 14 and 15; to emphasize these differences, note that, whereas stable silabutatrienes >Si=C=C=C< are still unknown,[62] phosphabutatrienes[29m,63] —P=C=C=C< or diphosphabutatrienes[63d,64] —P=C=C=P— have been synthesized and isolated.

— On going down the Periodic table, the stabilization is expected to be more and more difficult. For instance, tin and antimony allenic derivatives are rare or still unknown. It seems that the differences (chemical behavior and stability) between the Si and Ge allenes and between the P and As allenes are small, but they are greater between the Ge and Sn or between the As and Sb compounds.

Moreover, the cleavage of the Sn—C or Sb—C bonds occurs more easily than that of the E—C bonds (E = Si, Ge, P, As); this fact makes studies of tin and antimony compounds more complicated.

Many studies of heteroallenes have been performed but this field is still extremely rich and new types of very interesting structures remain to be obtained; note for example the recent synthesis of the first trisilaallene >Si=Si=Si< by Kira.[65] This result also shows that, even if heteroallenes with the heteroatoms in 1,3-position are easier to synthesize because of their greater thermodynamic stability compared to that of heteroallenes with the heteroatom in position 2, the latter can be prepared when the appropriate synthetic route and substituents will be found.

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