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Phosphasilaallenes  $>Si = C = P-$  and phosphagermaallenes  $>Ge = C = P-$ Phosphasilaallènes  $>Si=C=P-$  et phosphagermaallènes  $>Ge=C=P$ Jean Escudie<sup>a,\*</sup>, Gabriela Nemeş<sup>c</sup><sup>a</sup> UPS, LHFA, université de Toulouse, 118, route de Narbonne, 31062 Toulouse, France<sup>b</sup> CNRS, LHFA, UMR 5069, 31062 Toulouse cedex 09, France<sup>c</sup> Universitatea Babeş-Bolyai, Cluj-Napoca, Facultatea de Chimie și Inginerie Chimică, Arany-Janos, Nr.1, RO-400084, Romania

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to the memory of  
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## ABSTRACT

Phosphasilaallene  $\text{Tip(Ph)Si} = \text{C} = \text{PMes}^*$  (Tip = 2,4,6-triisopropylphenyl,  $\text{Mes}^* = 2,4,6$ -tri-*tert*-butylphenyl) and phosphagermaallene  $\text{Mes}_2\text{Ge} = \text{C} = \text{PMes}^*$  (Mes = 2,4,6-trimethylphenyl) have been obtained by dehalogenation of their corresponding dihalophosphametallapropenes  $>E(X)-C(X')=P-$  by *tert*-butyllithium. They dimerize above  $-40^\circ\text{C}$  by a cycloaddition involving two  $E = C$  double bonds or the  $E = C$  and the  $P = C$  double bonds but can be characterized at low temperature by trapping reactions and by low field shifts in  $^{31}\text{P}$ ,  $^{29}\text{Si}$  and particularly  $^{13}\text{C}$  NMR for the sp carbon atom. Owing to a small increase in the steric hindrance, phosphagermaallene  $\text{Tip}(t\text{-Bu})\text{Ge} = \text{C} = \text{PMes}^*$  can be stabilized and isolated. The  $\text{Ge} = \text{C}$  double bond undergoes nearly quantitative  $[2 + 1]$  cycloadditions with chalcogens and  $[2 + 2]$  cycloadditions with aldehydes or ketones. The surprisingly stable lithiochlorosilane  $\text{R}(\text{Cl}_2)\text{Si}-\text{C}(\text{Li}) = \text{PMes}^*$  (R = 9-methylfluorenyl) behaves as a synthetic equivalent of the phosphasilaallene  $\text{R}(\text{Cl})\text{Si} = \text{C} = \text{PMes}^*$ . With two alkyl groups (*t*-Bu) on the germanium atom, the phosphagermaallene  $t\text{-Bu}_2\text{Ge} = \text{C} = \text{PMes}^*$  is not obtained but its formal dimers 1,3-digermacyclobutanes have been isolated.

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## R É S U M É

Le phosphasilaallène  $\text{Tip(Ph)Si} = \text{C} = \text{PMes}^*$  (Tip = 2,4,6-triisopropylphényle,  $\text{Mes}^* = 2,4,6$ -tri-*tert*-butylphényle) et le phosphagermaallène  $\text{Mes}_2\text{Ge} = \text{C} = \text{PMes}^*$  (Mes = 2,4,6-triméthylphényle) transitoires ont été obtenus par déshalogénéation des dihalogénophosphamétallapropènes correspondants  $>E(X)-C(X')=P-$  par le *tert*-butyllithium. Ils se dimérisent au-dessus de  $-40^\circ\text{C}$  mais ont pu être caractérisés à basse température par réactions de piégeage et par des déplacements à champ faible en RMN du  $^{31}\text{P}$ , du  $^{29}\text{Si}$  et du  $^{13}\text{C}$  pour le carbone sp. Grâce à une faible augmentation de l'encombrement stérique, le phosphagermaallène  $\text{Tip}(t\text{-Bu})\text{Ge} = \text{C} = \text{PMes}^*$  a pu être stabilisé et isolé. Il réagit par la double liaison  $\text{Ge} = \text{C}$  en donnant des cycloadditions  $[2 + 1]$  avec les chalcogènes et  $[2 + 2]$  avec les aldéhydes et les cétones. Le lithiochlorosilane  $\text{R}(\text{Cl}_2)\text{Si}-\text{C}(\text{Li}) = \text{PMes}^*$  (R = 9-méthylfluorényle), qui présente une stabilité surprenante, se comporte comme un équivalent synthétique du phosphasilaallène  $\text{R}(\text{Cl})\text{Si} = \text{C} = \text{PMes}^*$ . Avec deux groupes alkyles (*t*-Bu) sur le germanium, le phosphagermaallène  $t\text{-Bu}_2\text{Ge} = \text{C} = \text{PMes}^*$  n'est pas obtenu mais ses dimères formels, les 1,3-digermacyclobutanes, ont été isolés.

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## 1. Introduction

For a long time, organophosphorus chemistry has been built on tricoordinate to hexacoordinate phosphorus compounds [1a]. In group 14, the organosilicon (or –germanium) chemistry has involved mainly tetracoordinate silicon and germanium. Whereas doubly-bonded compounds of the lightest elements of groups 14 and 15, such as alkenes or imines, have been very well studied and have proved to be major building blocks in organic chemistry owing to the reactivity of the double bond, the stable examples of their heavier counterparts were unknown. The first reports claiming the formation of such compounds (for example diphosphene  $\text{PhP}=\text{PPh}$  [1b], silene  $\text{Ph}_2\text{Si}=\text{CH}_2$  [1c]) appeared to be wrong. Thus, the “double bond rule”, which states that elements of the third or fourth row are unable to form stable double bonds has been postulated.

The success in the almost simultaneous synthesis of the first stable diphosphene  $\text{Mes}^*\text{P}=\text{PMe}_s^*$  by Yoshifuji et al. ( $\text{Mes}^* = 2,4,6\text{-tri-}t\text{-butylphenyl}$ ) [2], disilene  $\text{Mes}_2\text{Si}=\text{SiMe}_2$  by West et al. ( $\text{Mes} = 2,4,6\text{-trimethylphenyl}$ ) [3] and silene  $(\text{Me}_3\text{Si})_2\text{Si}=\text{C}(t\text{-Bu})\text{OSiMe}_3$  by Brook et al. [4] has demonstrated that the stabilization of such derivatives was possible by using sterically demanding organic substituents around the double bond preventing the approach of two molecules and thus their dimerization. Spectacular progress in this field of low coordinate derivatives has been achieved from the mid 1980s and now almost all combinations  $\text{E}_{14}=\text{E}_{14}$  [5],  $\text{E}_{14}=\text{E}_{15}$  [5a–b,5e,6–8] and  $\text{E}_{15}=\text{E}_{15}$  [5a,5i,9] ( $\text{E}_{14} = \text{Si, Ge, Sn}$ ;  $\text{E}_{15} = \text{N, P, As}$ ) have been obtained. In the field of compounds with a  $\text{E}=\text{C}$  double bond, following the synthesis of heavier analogues of alkenes,  $>\text{E}_{14}=\text{C}<$ , and imines,  $-\text{E}_{15}=\text{C}<$ , another challenge has been the synthesis of heavier analogues of allenes  $\text{E}=\text{C}=\text{E}'$ ; such derivatives are particularly interesting due to the presence of two cumulative double bonds but seemed more difficult to stabilize due to the two unsaturations.

The first heteroallenes were the phosphallaene  $\text{Mes}^*\text{P}=\text{C}=\text{CPh}_2$  [10] synthesized by Yoshifuji et al. in 1984 and the diphosphaallene  $\text{Mes}^*\text{P}=\text{C}=\text{PMe}_s^*$  [11] obtained the same year simultaneously by Appel, Yoshifuji

and Karsch by different methods (Scheme 1). Since this date, other allenic compounds of phosphorus of the type  $-\text{P}=\text{C}=\text{E}_{15}-$  ( $\text{E}_{15} = \text{N, As}$ ) or  $-\text{P}=\text{C}=\text{E}_{16}$  ( $\text{E}_{16} = \text{O, S}$ ) have been successfully isolated or characterized [12–17].

In the field of heavier group 14 elements, some silaallenes  $>\text{Si}=\text{C}=\text{C}<$  [12–18] and two germaallenes  $>\text{Ge}=\text{C}=\text{C}<$  [12–17,19] have been isolated and structurally characterized (Scheme 2) for the synthesis of the first representatives.

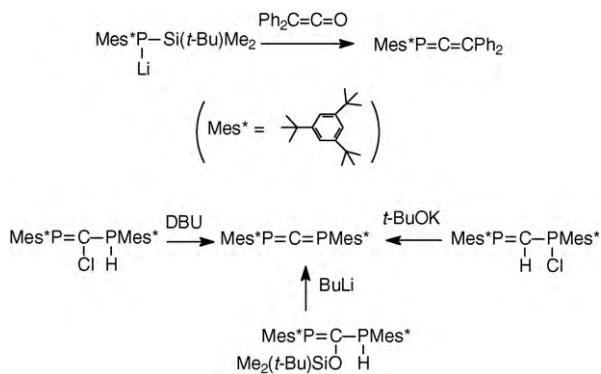
Owing to our experience on doubly-bonded compounds of phosphorus and germanium such as phosphagermenes  $-\text{P}=\text{Ge}<$  [20] and germenes  $>\text{Ge}=\text{C}<$  [21] and on synthetic equivalent of silenes  $>\text{Si}=\text{C}<$  [22] we have been particularly interested in studying heteroallenic compounds featuring double bonds on phosphorus and silicon or germanium of the types  $>\text{Si}=\text{C}=\text{P}-$  and  $>\text{Ge}=\text{C}=\text{P}-$ . Such compounds appear interesting from an academic point of view: many questions deserve an answer, such as the determination of the geometry (is it close to that of an allene or completely different, is the  $\text{P}=\text{C}=\text{Si}$  (or  $\text{Ge}$ ) angle of  $180^\circ$  and the dihedral angle around the double bond of  $90^\circ$ ), the charges (are the unsaturations polarized  $\text{P}^{\delta+}=\text{C}^{\delta-}$  and  $\text{Si}$  (or  $\text{Ge}$ ) $^{\delta+}=\text{C}^{\delta-}$  or is there a reverse polarity), the electronic configuration, the types of substituents (electron releasing or withdrawing) able to stabilize the double bonds, and on which element ( $\text{E}_{14}$  or  $\text{E}_{15}$ ) they are the most efficient. The study of their reactivity is also very interesting: does only one double bond react preferentially, and which one (even if the  $\text{E}_{14}=\text{C}$  double bond is suspected to be more reactive than the  $\text{E}_{15}=\text{C}$  double bond) or do both double bonds react? It is also possible to imagine the reactivity of the lone pair at phosphorus and the cleavage of the  $\text{Si}=\text{C}$  (or  $\text{Ge}=\text{C}$ ) double bond to silylene  $>\text{Si}$  (or germylene  $>\text{Ge}$ ) and  $\text{C}=\text{P}-$ . Thus, such compounds are promising as building blocks in organophosphorus and organometallic chemistry, as precursors of polymers and as ligands.

This short review describes theoretical studies, synthesis, physicochemical characterizations and the reactivity of phosphasilaallenes  $>\text{Si}=\text{C}=\text{P}-$  and phosphagermaallenes  $>\text{Ge}=\text{C}=\text{P}-$ .

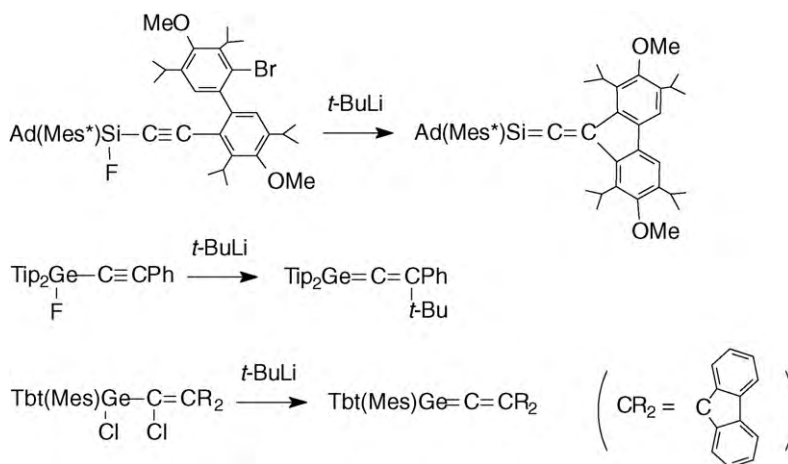
## 2. Results and discussion

### 2.1. Theoretical calculations

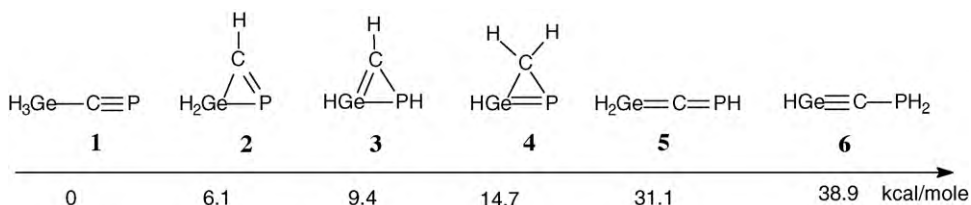
Calculations (B3LYP/6-31G(d,p)) have been carried out on the parent compound  $\text{H}_2\text{Ge}=\text{C}=\text{PH}$  and its isomers of  $\text{H}_3\text{CGeP}$  formula [23] (Scheme 3). Among the structures with a  $\text{PCGe}$  linkage 1–6, the most stable isomer is, as expected, the triple bond  $\text{P}\equiv\text{C}$  compound 1 (many phosphaaalkynes have been isolated [24,25]). Three phosphagermirenes 2, 3 and 4 are more stable than phosphagermaallene 5, which lies 31.1 kcal/mol higher than phosphaaalkyne 1. Note that the three-membered ring compound 7 (Fig. 1), analogous to 2, has been isolated by reaction between a germylene and a phosphaaalkyne [26]. The triple bond  $\text{Ge}\equiv\text{C}$  derivative 6 is the least stable, which is not surprising since no stable germyne has been reported until now.



Scheme 1.



Scheme 2.



Scheme 3.

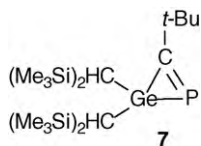


Fig. 1. Structure of compound 7.

The main geometrical parameters (Ge=C and P=C bond lengths and GeCP bond angle) have been calculated at two levels of theory: CCSD/6-31G(d,p) Ge=C = 1.784 Å, P=C = 1.648 Å, GeCP = 164.04° and MP4(SDQ)/6-31G(d,p) Ge=C = 1.789 Å, P=C = 1.650 Å, GeCP = 162.56° [23]. They are in good agreement with the parameters recently determined by X-ray: Ge=C = 1.761(2) Å, P=C = 1.625(2) Å, GeCP = 166.55(14)° (unpublished results).

From this study it can be supposed that the stabilization of a phosphagermaallene >Ge=C=P- is not obvious; like in the case of other heteroallenes, the choice of the substituents at the germanium and phosphorus atoms is probably extremely important for this stabilization.

## 2.2. Transient phosphagermaallene and phosphasilaallene

### 2.2.1. General procedure

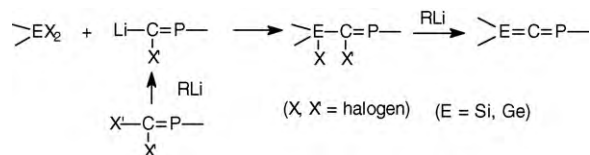
From our experience on silenes and germenes >E=C< (E = Si, Ge) [21,22] and the results of the literature [10,11] it

appeared that the E=C double bond should be probably more reactive than the P=C double bond. Thus, the best strategy to synthesize a phosphagerma- (or -sila) allene was to create first the P=C double bond since the simultaneous formation of both double bonds seems unlikely. Thus, the general procedure is presented in Scheme 4.

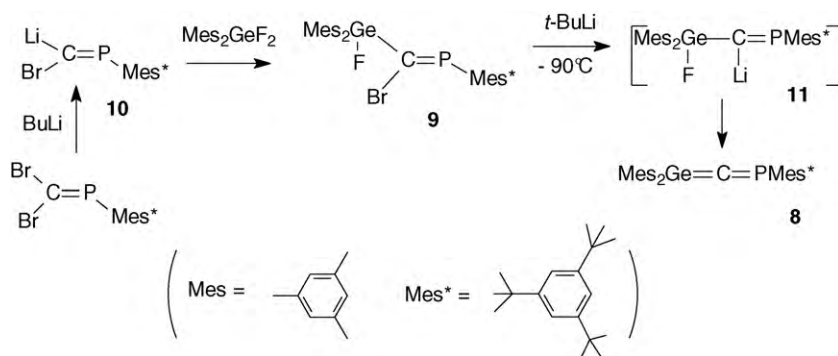
### 2.2.2. Phosphagermaallene 8

The 2,4,6-tri-*tert*-butylphenyl group, called supermesityl (Mes\*), widely used to stabilize doubly bonded phosphorus compounds, was chosen on the phosphorus atom. As mesityl groups (Mes = 2,4,6 trimethylphenyl) were very efficient to stabilize the germene Mes<sub>2</sub>Ge = CR<sub>2</sub> (CR<sub>2</sub> = fluorenylidene) [21a–b] they were chosen on the germanium atom.

In order to avoid side reactions, particularly reduction of the Ge-X bond or alkylation (by the lithium compound), fluorine was preferred to chlorine as halogen on the germanium atom. Moreover the <sup>19</sup>F NMR allowed us to monitor the reaction.



Scheme 4.



Scheme 5.

Phosphagermapropene **9** [27a], precursor of phosphagermaallene **8**, was synthesized by a coupling reaction between the phosphacarbene  $\text{Mes}^*\text{P}=\text{C}(\text{Br})\text{Li}$  **10** [28] and difluorodimesitylgermane in the form of only one geometrical isomer ( $\delta^{31}\text{P} = 321.3$  ppm,  $^3J_{\text{PF}} = 29.8$  Hz). We postulate it to be the *Z* isomer due to the selective lithium/bromine exchange of the bromine atom in  $\text{Mes}^*\text{P}=\text{CBr}_2$  that is in *trans* in relation to the huge  $\text{Mes}^*$  group as previously reported in the literature on similar compounds [28].

Addition of *t*-BuLi to an  $\text{Et}_2\text{O}$  solution of **9** led to the immediate formation of the lithium compound **11** ( $\delta^{31}\text{P} = 397.4$  ppm,  $^3J_{\text{PF}} = 16.9$  Hz) [27a]. Elimination of LiF was observed at  $-60^\circ\text{C}$  leading to an orange solution of the expected phosphagermaallene **8** in about 70% yield [27a] (Scheme 5).

Phosphagermaallene **8** was characterized by a low-field shift in  $^{31}\text{P}$  NMR (240.0 ppm) and particularly in  $^{13}\text{C}$  NMR (280.9 ppm,  $^1J_{\text{CP}} = 54.3$  Hz for the *sp* carbon atom) [27a]. Similar low-field chemical shifts have been reported for the *sp* carbon atom in other heteroallenes:  $\text{Mes}^*\text{P}=\text{C}=\text{AsMes}^*$  (299.5 ppm) [29],  $\text{Tip}_2\text{Ge}=\text{C}=\text{C}(\text{Ph})t\text{-Bu}$  (235.1 ppm) [19a] (Tip = 2,4,6-triisopropylphenyl) and  $\text{Tbt}(\text{Mes})\text{Ge}=\text{C}=\text{CR}_2$  (243.5 ppm) [19b] (Tbt = 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl,  $\text{CR}_2 = \text{fluorenylidene}$ ).

Heteroallene **8** was stable only below  $-40^\circ\text{C}$  and warming to room temperature led to dimers (section 2.2.4).

### 2.2.3. Phosphasilaallene **12**

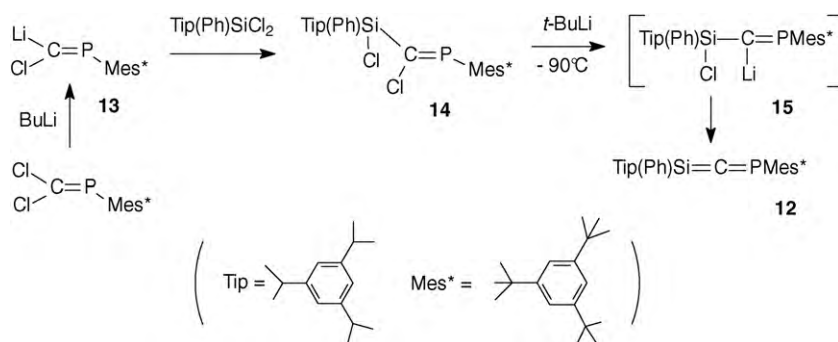
Using the same mesityl groups on silicon failed to afford the phosphasilaallene analogue. The coupling reaction of

$\text{Mes}_2\text{SiF}_2$  with the phosphacarbene  $\text{Mes}^*\text{P}=\text{C}(\text{Br})\text{Li}$  **10** occurred with a poor yield due to the too large steric congestion hindering the approach of the two reagents. Thus, Tip (2,4,6-triisopropylphenyl) and Ph groups were used, the presence of a small group like phenyl allowing the coupling to form the phosphasilapropene  $\text{Tip}(\text{Ph})\text{Si}(\text{F})\text{C}(\text{Br})=\text{PMes}^*$ . However, even in this case, the coupling was difficult, the main product being the phosphaaalkyne  $\text{Mes}^*\text{C}\equiv\text{P}$  resulting from the decomposition around  $-80^\circ\text{C}$  of **10**, before its reaction with the difluorosilane, followed by a rearrangement. Thus, its much more stable chlorine analogue  $\text{Mes}^*\text{P}=\text{C}(\text{Cl})\text{Li}$  **13** [30] was used.

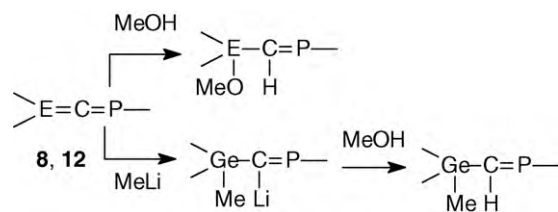
Phosphasilaallene **12** [31] was obtained by dechlorination of phosphasilapropene **14** by *tert*-butyllithium at  $-90^\circ\text{C}$  in a mixture toluene/ $\text{Et}_2\text{O}$  90/10 (Scheme 6). The intermediate formation of the lithium compound **15** was evidenced in  $^{31}\text{P}$  NMR by the very low-field shift (417.6 ppm) characteristic of the presence of two electropositive elements (Si and Li) on the *sp*<sup>2</sup> carbon atom and by hydrolysis leading to  $\text{Tip}(\text{Ph})(\text{Cl})\text{Si}-\text{C}(\text{H})=\text{PMes}^*$  [31].

The formation of phosphasilaallene **12** was proved by its low-field shift in  $^{31}\text{P}$  (288.7 ppm),  $^{13}\text{C}$  (269.1 ppm,  $^1J_{\text{CP}} = 45.8$  Hz) and  $^{29}\text{Si}$  NMR (75.7 ppm,  $^2J_{\text{SiP}} = 18.3$  Hz).  $^{13}\text{C}$  and  $^{29}\text{Si}$  chemical shifts are comparable to those observed in silaallenes  $\text{Ad}(\text{Mes}^*)\text{Si}=\text{C}=\text{CR}_2$  ( $\text{CR}_2 = \text{substituted fluorenylidene}$ ) (225.7 and 48.4 ppm) [18a] and *t*-Bu( $\text{Mes}^*$ )- $\text{Si}=\text{C}=\text{C}(\text{Ph})t\text{-Bu}$  (216.3 and 55.1 ppm) [18b].

Like its germanium analogue, phosphasilaallene **12** was stable only below  $-30^\circ\text{C}$  and dimerized above this temperature (section 2.2.4).



Scheme 6.



Scheme 7.

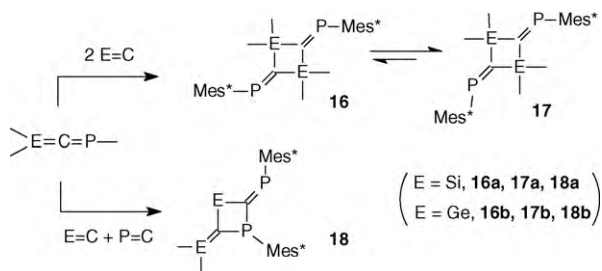
#### 2.2.4. Reactivity

Heteroallenes **8** and **12** reacted nearly quantitatively with methanol and phosphagermaallene **8** with methyl-lithium. These additions occurred exclusively onto the E=C double bond, according to the expected  $E^{\delta+}=C^{\delta-}$  polarity and led to the sole *E*-phosphaalkenes (Scheme 7).

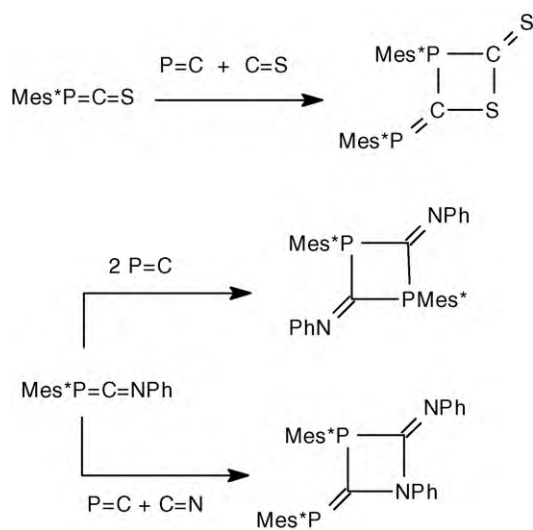
In the absence of trapping reagent, phosphasilaallene **12** and phosphagermaallene **8** give two types of dimers: the expected head-to-tail dimers **16** and **17** and the unsymmetrical dimer **18** [27a,31] (Scheme 8). 1,3-Dimetalcyclobutanes **16** and **17**, containing two exocyclic P=C double bonds, are obtained by dimerization involving two E=C double bonds; a dynamic equilibrium is observed between the dimers **16** and **17**; according to the NMR analysis, the major one is **17** with the two Mes\* groups in *cis* disposition in relation to the P=C...C=P axis; this assumption was proved in the case of the silicon compound **17a** by an X-ray analysis which displays a nearly planar four-membered ring [31]. Very low-field chemical shifts in  $^{31}\text{P}$  NMR are observed for **16** and **17** particularly for the silicon compounds (trans 431.9 and *cis* 425.4 ppm) due to the presence of two silicon atoms onto the  $sp^2$  hybridized carbon atom [31].

Dimers **18** were formed by a cycloaddition between E=C and P=C double bonds and are the major ones (E=Si: **18a** 60%, **16a/17a** 40% [31], E=Ge: **18b** 88%, **16b/17b** 12% [27a]). They were characterized by two doublets in  $^{31}\text{P}$  NMR: **18a** = 294.9 and 86.9 ppm ( $^2J_{\text{PP}}$  = 224 Hz); **18b** = 269.5 and 69.3 ppm ( $^2J_{\text{PP}}$  = 225.4 Hz). According to the large PP coupling constant, it seems that the isomer obtained has the lone pair on the  $\lambda^3\sigma^2$  P in *trans* disposition in relation to the  $\lambda^3\sigma^3$  P atom since the literature reports that  $^2J_{\text{PP}}$  is 15–30 Hz in *cis* structures but much larger (more than 100 Hz) in *trans* structures [32].

The unsymmetrical dimerization seems a priori surprising but is not so unexpected since it has been reported to occur in other phosphaallenic derivatives such as



Scheme 8.



Scheme 9.

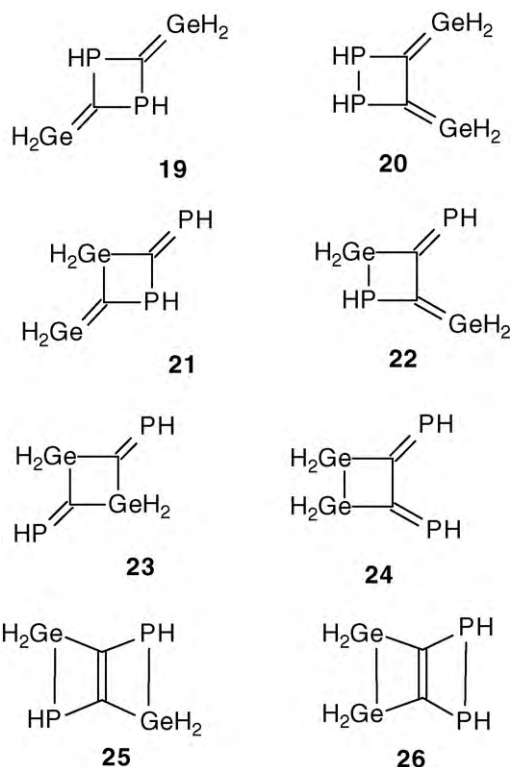
phosphatioketene  $\text{Mes}^*\text{P}=\text{C}=\text{S}$  [33]. Both types of dimerization occur in phosphaazaallenes  $\text{Mes}^*\text{P}=\text{C}=\text{NPh}$  depending on the experimental conditions [34] (Scheme 9).

To have a rough idea about the relative stability of the dimers of parent compound  $\text{H}_2\text{Ge}=\text{C}=\text{PH}$ , calculations have been performed [27a] (restricted Hartree-Fock calculations using Gaussian 92 package: for C, P and Ge atoms, effective core potentials were used [27b]; for all atoms the valence atomic basis sets consist of four Gaussian functions contracted to a double- $\zeta$  level and augmented by a polarization function; the geometries have been optimized by using a gradient technique). As expected, due to the greater stability of the P=C than Ge=C double bond, the dimers between two P=C double bonds **19** and **20** lie 25 kcal/mol above dimers **21** and **22** formed by Ge=C and P=C cycloadditions (Scheme 10). Dimers **23** and **24** formed from two Ge=C double bonds are normally more favourable by 18 kcal/mol [27a]. Only analogous of **21** and **23** have been experimentally observed because the formation of **22** and **24** is unfavorable due to the steric hindrance caused by the Mes and Mes\* groups.

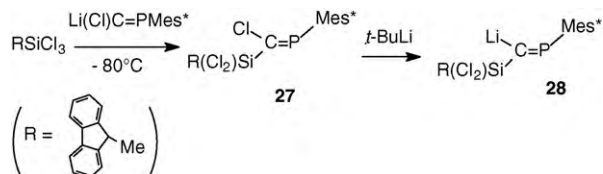
The most stable dimers are the butterfly structures **25** and **26**. These bicyclic derivatives were calculated to lie 15 kcal/mol below **23** and **24**. However, the formation of such structures, arising from **22** and **24** by a second cycloaddition between one Ge=C and one P=C or two P=C double bonds, are not possible with large groups at the germanium and phosphorus atoms.

#### 2.3. Chlorosilylphosphaethenyllithium

In order to increase the synthetic utility of phosphasilaallene, we tried to attach at the silicon atom a chlorine atom which could allow functionalisation of the Si=C=P system. The other group at Si was a 9-methylfluorenyl group intended to provide extrasteric protection for the Si=C double bond. The trichlorophosphasilapropene **27**



Scheme 10.

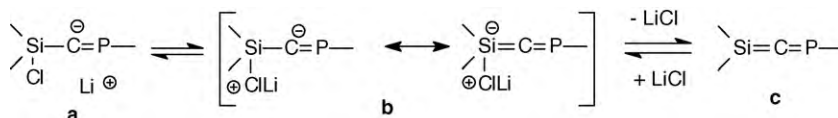


Scheme 11.

[35] was prepared by the same routes as dichlorophosphasilapropene **14** by coupling phosphacarbenoid **13** with dichloro(9-methylfluorenyl)silane (Scheme 11).

The  $^{31}\text{P}$  NMR analysis displayed, as previously, the formation of only one isomer ( $\delta = 328.1$  ppm). The X-ray analysis confirmed the formation of the *Z* isomer due to the selective lithium/chlorine exchange of the chlorine atom in *trans* in relation to the huge  $\text{Mes}^*$  group.

Treatment of **27** with *tert*-butyllithium resulted in the formation of the expected lithium compound **28** which was evidenced by a very low-field chemical shift in  $^{31}\text{P}$  NMR (441.4 ppm) and by hydrolysis with one equivalent of water leading to  $\text{RCl}_2\text{SiC(H)=PMes}^*$  [35] (Scheme 11).



Scheme 12.

Surprisingly, whereas the elimination of lithium halide occurred at low temperature in the case of **15** and **11** substituted at Si and Ge by aryl groups, no elimination was observed in the case of **28**.

Calculations on the  $[\text{Cl}_{3-n}\text{H}_n\text{Si-C=PH}]^-$  anion at the RHF/6-31 + G\*\* level show that the increasing number of chlorine atoms at the silicon increases the negative charge (natural charges) on the central carbon from  $-1.224$  ( $n = 3$ ) to  $-1.393$  ( $n = 0$ ) [35]. This is in favour of form **a** whereas form **b** should be necessary to form the double bond (Scheme 12), according to a study of Wiberg on compounds of the type  $\text{Si(X)-C(Li)}$  [36].

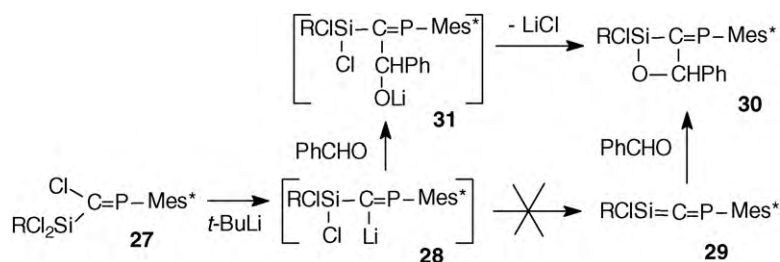
To have a better understanding about the non elimination of LiCl, molecular orbital calculations (RHF/3-21G\* level) have been carried out to determine the relative stability of the conformers of the simplified system  $\text{Cp}'\text{Cl}_2\text{Si-C(Li)=PMes}^*$  ( $\text{Cp}' = 1\text{-methylcyclopentadienyl}$ ). The most stable isomer shows a strong interaction between the lithium atom and the  $\pi$  systems of  $\text{Mes}^*$  and  $\text{Cp}'$  with short distances between Li and the centroid of these aromatic systems. This lithium- $\pi$  interaction also favours form **a**.

However, the chlorosilyllithium **28** can be considered as a synthetic equivalent of the phosphasilaallene **29**; for example, reaction with benzaldehyde afforded the oxasiletane **30** probably via the intermediate **31** followed by cyclization (Scheme 13); reaction between the phosphasilaallene **29** and benzaldehyde should presumably give the same four-membered ring compound **30** by a [2 + 2] cycloaddition between the  $\text{Si=C}$  and  $\text{C=O}$  double bonds as in the case of a stable phosphagermaallene and benzaldehyde (section 2.5).

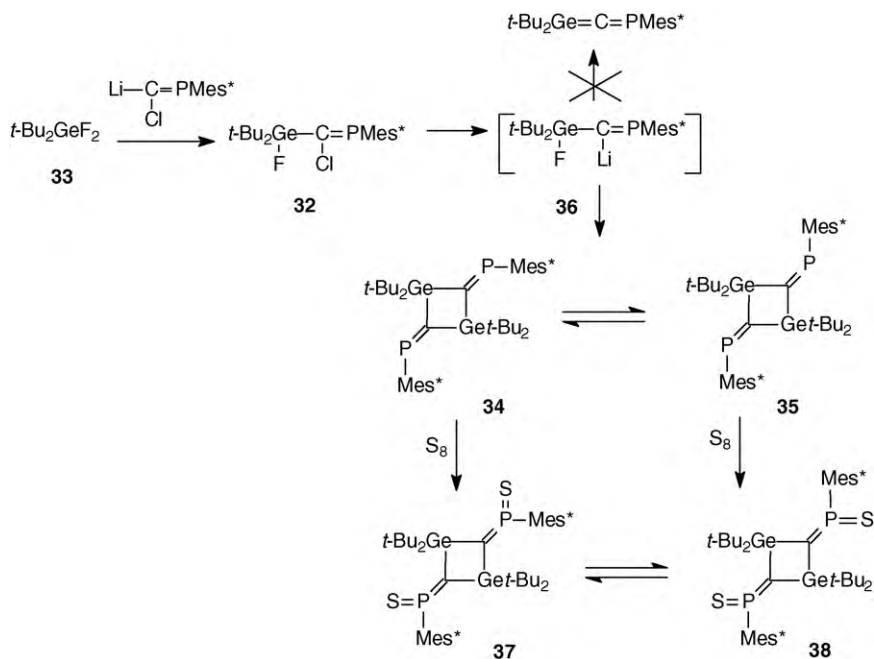
#### 2.4. 2,4-Diphosphenylidene-1,3-digermacyclobutanes

The replacement on the germanium atom of the two mesityl groups by two *t*-Bu groups which present a steric hindrance more important close to the germanium atom than  $\text{Mes}$  groups could theoretically prevent the dimerization of the  $\text{Ge=C}$  double bond.

In fact, addition of *t*-BuLi to the phosphagermapropene **32** [37] (formed from difluorogermane **33** and phosphacarbenoid  $\text{Mes}^*\text{P=C(Cl)Li}$ ), did not lead to the expected phosphagermaallene  $t\text{-Bu}_2\text{Ge=C=PMes}^*$ , but to its formal dimers, the 2,4-diphosphenylidene-1,3-digermacyclobutanes **34** and **35** as two isomers with exocyclic  $\text{P=C}$  double bonds ( $\delta^{31}\text{P} = 367.4$  and  $367.7$  ppm for the *cis* and *trans* isomers in relation to the  $\text{P-C}\cdots\text{C-P}$  axis) [37] (Scheme 14). Owing to their different solubilities (the *cis* isomer **34** has a non-zero dipole moment and thus a better solubility in polar solvents) both isomers have been purified by crystallization and characterized by an X-ray structure.



Scheme 13.



Scheme 14.

Monitoring the reaction by  $^{31}\text{P}$  NMR from  $-80^\circ\text{C}$  to  $20^\circ\text{C}$  did not evidence the expected phosphagermaallene  $t\text{-Bu}_2\text{Ge}=\text{C}=\text{P}(\text{Mes}^*)$ , but an intermediate ( $\delta^{31}\text{P}=286.7$  and  $443.8$  ppm,  $J_{\text{PP}}=38.5$  Hz) probably resulting from an intermolecular condensation between two molecules of **36** with loss of  $\text{LiF}$  instead of the expected intramolecular elimination to give the heteroallene.

Thus, this reaction is completely different of that observed in the case of **11** and **8** (Mes groups on Ge) and it seems that at least one aryl group on the metal atom is necessary to cause the intramolecular elimination of lithium halide to take place and to form the heteroallene.

Note that reaction of **34** and **35** with an excess of sulphur afforded the first bis(methylenethio)phosphoranes **37** and **38** with two  $\text{C}=\text{P}(\text{S})\text{Mes}^*$  units [37] (Scheme 14).

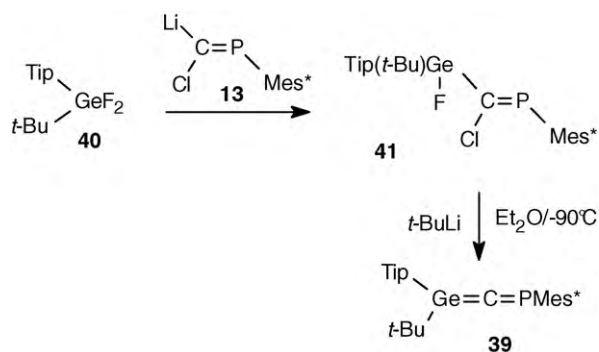
## 2.5. Stable phosphagermaallene 39

### 2.5.1. Synthesis and physicochemical data

From the experience gained in the previous attempts, it seemed that a combination of one aromatic group (Tip)

and one alkyl group ( $t\text{-Bu}$ ), which presents the advantage of a large steric hindrance at long distance (Tip) and short distance ( $t\text{-Bu}$ ) of the germanium atom, could be successful to stabilize a phosphagermaallene. Difluorogermane **40** [38] was obtained from  $\text{TipGeCl}_3$  [39] via the methoxy compounds  $\text{TipGe}(\text{OMe})_3$  and  $\text{Tip}(t\text{-Bu})\text{Ge}(\text{OMe})_2$ . Reaction of **40** with the phosphacarbene **13** led to **41**, the expected precursor of the phosphagermaallene. The great steric hindrance in **41** was clearly evidenced in the  $^1\text{H}$  NMR spectrum by the presence of two signals for the  $o\text{-}t\text{-Bu}$  groups of  $\text{Mes}^*$  and a very large one for the methyls of the  $o\text{-}i\text{Pr}$  groups due to their slow rotation on the NMR time scale. Only one isomer was observed, probably the *Z*-isomer as demonstrated previously in similar reactions. Addition of one equivalent of *tert*-butyllithium to an  $\text{Et}_2\text{O}$  solution of **41** at  $-90^\circ\text{C}$  led to the nearly quantitative formation of phosphagermaallene **39** [38] (Scheme 15).

Red-brown solutions of **39** are extremely air and moisture sensitive, but no change was observed for months in an inert atmosphere. Crystallization in a sealed tube afforded orange crystals.



Scheme 15.

**39** is the first stable heteroallenic compound with two heavy group 14 and 15 elements. Thus, a rather small change in the substitution at the germanium atom (Tip and *t*-Bu instead of two mesityl groups) changed drastically the stability of the heteroallene.

The structure of **39** was proved by a low-field shift in  $^{31}\text{P}$  NMR (250 ppm) and particularly in  $^{13}\text{C}$  NMR for the central *sp* carbon atom (280.4 ppm,  $J_{\text{PC}} = 60.9$  Hz) [38] comparable to that previously reported for transient phosphagermaallene **8** and phosphasilaallene **12**.

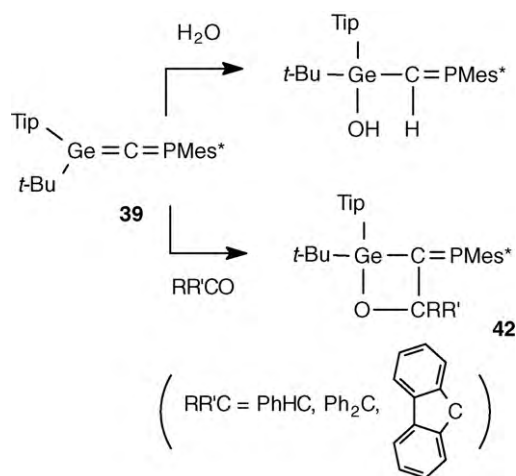
### 2.5.2. Reactivity

The structure of **39** was also proved by its chemical reactivity. A regioselective addition of water on the Ge=C double bond occurred, with the hydroxy moiety bonded to the germanium atom because of the  $\text{Ge}^{\delta+}-\text{C}^{\delta-}$  polarity of the double bond [38] (Scheme 16). The addition is also stereoselective, but it was impossible from the  $^2J_{\text{PH}}$  coupling constant (25.0 Hz) to determine the configuration of the reaction product (in the similar C-germylphosphaalkene  $\text{Me}_3\text{GeC(H)=PMes}^*$  [28a], the  $^2J_{\text{PH}}$  constants are 26.4 and 23.5 Hz for the *E* and *Z* isomers, respectively).

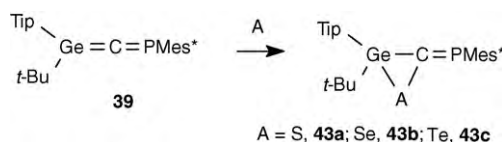
With aldehydes (benzaldehyde) and non-enolizable ketones (benzophenone and fluorenone), [2 + 2] cycloadditions between the Ge=C and C=O unsaturations occurred leading to oxagermetanes **42** with an exocyclic P=C double bond [38] (Scheme 16).

[2 + 1] cycloadditions on the Ge=C double bond occurred with chalcogens: addition of sulphur, selenium or tellurium led to the chalcogenagermiranes **43** [40] (Scheme 17). Such 3-membered ring compounds are very stable, probably owing to the large steric hindrance. With one equivalent of chalcogen, only the cycloadduct involving the Ge=C double bond was formed showing the greater reactivity of this unsaturation than that of the lone pair on phosphorus which is generally very reactive towards chalcogens. The presence of the exocyclic P=C double bond is evidenced in  $^{31}\text{P}$  NMR by the classic low-field shift (**43a**: 252.2, **43b**: 278.8, **43c**: 311.8 ppm). The PSe (107.5 Hz) and PTe (249.6 Hz) coupling constants are larger than those found for selenadiphospholes (50–80 Hz) and telluradiphospholes (130–150 Hz).

Surprisingly, **43b** and **43c** present a different configuration around the P=C double bond: *Z* for **43c** (Mes\* group *cis* to Te) and *E* for **43b** (Mes\* group *trans* to Se). The origin for this opposite arrangement is not clear at the moment.



Scheme 16.



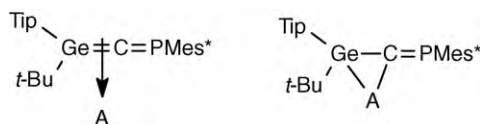
Scheme 17.

Another striking feature was discovered from the X-ray structure: for **43b** and **43c** the sum of angles on germanium is close to  $360^\circ$  (**43b**  $358.6^\circ$ , **43c**  $353.5^\circ$ ) [40] with a short Ge-C bond (1.912.6 Å in **43c**) in relation to the standard Ge-C bond length (1.96–1.98 Å) [41]. This partially planar geometry corresponds to a structure intermediate between a  $\pi$ -complex and a normal three-membered ring (Scheme 18).

These results can be interpreted in terms of Dewar-Chatt-Duncanson model of metal olefin bonding. Similar results have been reported in other three-membered ring compounds containing one germanium atom such as GePS [42] or GeCTe [43] or two germanium atoms GeGeX (X = C, N, S, Te) [44–46].

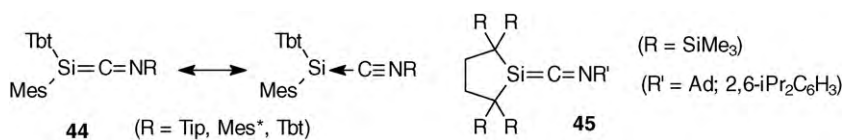
### 2.5.3. Comparison with SiCN derivatives

A completely different behaviour is observed between sila- (or germa)heteroallenes of nitrogen and phosphorus:  $>\text{Si}=\text{C}=\text{P}-$  and  $>\text{Ge}=\text{C}=\text{P}-$  keep their skeleton integrity in all the reactions studied and never behave as silylenes or germylenes  $>\text{E}$  and isophosphanitriles:  $\text{C}=\text{P}-$ . By a sharp contrast, most of the  $>\text{Si}=\text{C}=\text{N}-$  compounds are better described as complexes between silylenes and isonitriles  $\text{C}=\text{N}-$  (for example high field  $^{29}\text{Si}$  resonance from  $-48$  to  $-58$  ppm in **44**) [47]; however, **45** presents physicochemical



Scheme 18.





Scheme 19.

data ( $^{29}\text{Si}$  resonance at lower field: 15.9 and 23.9 ppm, short SiC bond, CN distance longer than that of aryl isocyanide) convenient for an azaphosphaallene structure [48] but also dissociates in solution above  $-30^\circ\text{C}$  (Scheme 19).

### 3. Conclusion and prospects

Transient phosphasilaallene  $\text{Tip}(\text{Ph})\text{Si}=\text{C}=\text{PMes}^*$  and phosphagermaallene  $\text{Mes}_2\text{Ge}=\text{C}=\text{PMes}^*$  have been characterized at low temperature and the first stable heteroallene with two heavy elements of groups 14 and 15, the phosphagermaallene  $\text{Tip}(t\text{-Bu})\text{Ge}=\text{C}=\text{PMes}^*$  has been isolated. This study shows the great difficulty to obtain stable doubly-bonded compounds of this type: with a too large steric hindrance on Si and Ge the coupling reaction between the dihalosilane (or -germane)  $\text{R}_2\text{EX}_2$  and the phosphacabenoid  $\text{Li}(\text{X})\text{C}=\text{P}-$  does not occur and with a low steric hindrance the final heteroallene dimerizes. Moreover, depending on the substituents at the metal, elimination of lithium halide sometimes does not occur, or gives directly a formal dimer of the phosphametallaallene by an intermolecular condensation with loss of lithium halide without the formation of the expected phosphametallaallene. Thus, the choice of the substituents is extremely crucial and difficult. It seems that at least one aryl group on Si (or Ge) is necessary.

With  $\text{E}_{14}$  and  $\text{E}_{15}$  belonging to the same row,  $\text{E}_{14}=\text{C}$  double bond appears to be much more reactive than  $\text{E}_{15}=\text{C}$  one. For example the phosphagermaallene **39** is much more reactive than its arsenic analogue  $\text{Mes}^*\text{As}=\text{C}=\text{PMes}^*$  [29]. Thus, the study of its chemical behaviour appears very promising.

A new challenge is to prepare phosphastannaallenes  $>\text{Sn}=\text{C}=\text{P}-$ . A very large steric hindrance on the tin atom will be necessary in order to prevent the dimerization of the  $\text{Sn}=\text{C}$  double bond, much longer than the  $\text{Ge}=\text{C}$  one. Until now, no tin heteroallene has been isolated. Stannaallene  $\text{Tip}_2\text{Sn}=\text{C}=\text{CR}_2$  ( $\text{CR}_2 = \text{fluorenylidene}$ ) has been postulated as intermediate in a reaction leading to a distannirane [49] and  $\text{R}_2\text{Sn}=\text{C}=\text{Mes}$  is like  $>\text{Si}=\text{C}=\text{N}-$  compounds better considered as a complex between stannylene  $\text{R}_2\text{Sn}$  and isonitrile:  $\text{C}=\text{NMe}_3$  than as an azastannaallene [50].

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