

Reviews

Group 14 and 15 Heteroallenes $E=C=C$ and $E=C=E'$

Jean Escudié* and Henri Ranaivonjatovo

Hétérochimie Fondamentale et Appliquée, UMR 5069, Université Paul Sabatier, 118 route de Narbonne, 31062 Toulouse Cedex 09, France

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This review describes the synthesis, physical properties, and some aspects of the reactivity of heteroallenes, namely the heavier congeners of allenes containing one or two doubly bonded heavier elements of groups 14 (Si, Ge, Sn) and 15 (P, As, Sb). The key factor for their preparation lies in the use of synthetic methods effective under mild conditions: i.e., in many cases, the dehalogenation at low temperature of dihaloheteropropenes by lithium derivatives. Their stabilization was successful, owing to very bulky substituents; substituted aromatic groups were often used, particularly the 2,4,6-tri-*tert*-butylphenyl group (supermesityl). Whereas various types of heteroallenes containing a doubly bonded element of the second or third long row have been isolated, their heavier counterparts of the fourth row have only been postulated as reaction intermediates.

Introduction

Alkenes are fundamental derivatives in organic chemistry, due to the ability of the $C=C$ double bond to lead to new organic functions by undergoing various addition or cycloaddition reactions, oxidations, and formations of triple bonds by elimination reactions.

The pioneering work of Yoshifuji on diphosphenes $-P=P-$,¹ Brook on silenes $>Si=C<$,² and West on disilenes $>Si=Si<$ ³ in 1981 proved that it was possible to stabilize the heteroalkenes $E=C$ and $E=E'$ ($E, E' = Si, Ge, Sn, P, As, Sb$), derivatives in which one or two doubly bonded carbon atoms have been replaced by heavier elements of group 14 and 15, owing to a large steric hindrance to prevent their dimerization. Due to their greater reactivity and the marked difference in their properties compared to those of the corresponding carbon compounds, heteroalkenes have attracted much attention for the last two decades, and almost all $E=E'$ combinations have been obtained.^{4–8}

Various kinds of substituents have been used to stabilize compounds with low-coordinate group 14 and 15 elements.⁹ One of the most popular is the 2,4,6-tri-*tert*-butylphenyl group (called supermesityl and abbreviated as Mes*), which is excellent in terms of steric protection and is easy to prepare in large quantities. Many other phenyl groups substituted at the 2,4,6-positions by various groups have been used, as well as 2,6-diarylphenyl (terphenyl) groups. Bulky alkyl groups such as adamantyl, triptyceny, bis(trimethylsilyl)methyl, and tris(trimethylsilyl)methyl also have proven to be efficient.

Sterically demanding silyl groups such as trimethylsilyl, tris(trimethylsilyl)silyl, tris(tri-*tert*-butylsilyl)silyl, and bis(di-*tert*-butylmethyl)silyl have been very effective at stabilizing various

types of doubly and even triply bonded species. Due to the electropositivity of the silicon atom, the nature of the double bond (polarity, bond lengths and angles, bending) was changed compared to that of heteroalkenes substituted by aryl or alkyl groups.

Intramolecular coordination of the electron-accepting part of the molecule by amino groups is also a solution for the stabilization of doubly bonded compounds.

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The less explored electronic effect also contributes to the stabilization, and groups such as tris(trifluoromethyl)phenyl and 2,6-bis(trifluoromethyl)phenyl are effective for both their steric and electronic effects.

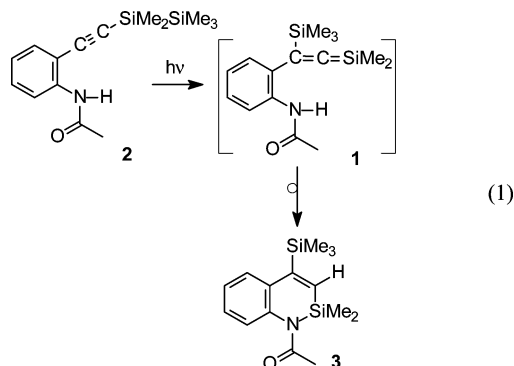
The synthesis of heteroallenes,¹⁰ compounds in which one, two, or even three carbon atoms of an allene have been replaced by heavier elements of group 14 or 15, have constituted a new challenge in organometallic chemistry. Such compounds, due to their unique structure, are very interesting from both academic and applied points of view. For example, X-ray structural studies should be important for two crucial points: the bending angle at the central sp carbon atom, which measures the deviation from linearity of the E=C=E' skeleton, and the sum of the bond angles around E and E', which measures their degree of pyramidalization. The determination of these geometrical parameters should allow an understanding of the bonding in these systems and allow estimation of how close to wholly organic allenes they are. The comparison between heteroallenes E₁₄=C=C and E₁₅=C=C, E₁₄ and E₁₅ belonging to the same row and being along the series Si → Sn and P → Sb, should also give important information on the bonding. Due to the presence of two unsaturations, such heteroallenes E=C=E' were thought to possess a rich and versatile chemistry and to be very useful building blocks in organometallic chemistry.

Here, we describe the synthesis, the physical properties, and some aspects of the reactivity of heteroallenes E=C=E'. For each category of heteroallenes, emphasis is placed on those synthesized in our group, such as the stannaallenes >Sn=C=C<, arsaallenes -As=C=C<, and stibaallenes -Sb=C=C< in the series >E₁₄(or -E₁₅)=C=C<, the diphosphaallenes -P=C=P- (with one σ²-, and σ³-phosphorus atom), phosphoarsaallenes -As=C=P- and diarsaallenes -As=C=As- in the series -E₁₅=C=E'₁₅-, and the phosphosilaallenes >Si=C=P- and phosphagermaallenes >Ge=C=P- in the series >E₁₄=C=E₁₅. We will finish this review by reporting the results in the field of heteroallenes with three heavy elements of group 14, the trimetallaallenes E₁₄=E₁₄=E₁₄. As heteroallenes were reviewed in 2000,^{10a} we will summarize the results reported by other groups before this date.

Silaallenes and Germaallenes >E₁₄=C=C< (E₁₄ = Si, Ge)

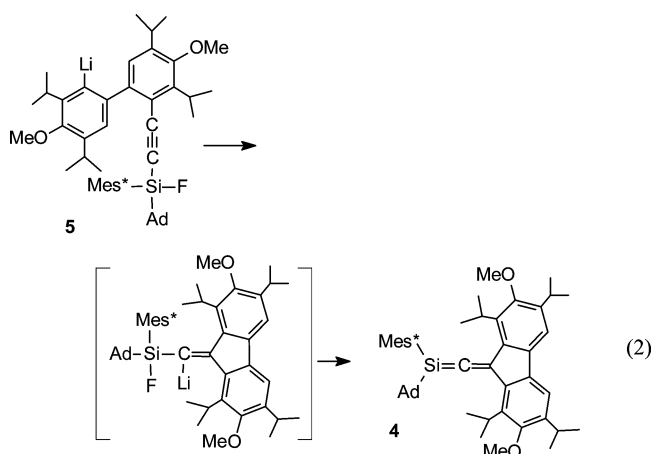
Many studies have been performed by Ishikawa et al., and more recently by other authors, on transient 1-silaallenes, which were obtained by photolysis or thermolysis of silirenes or ethynylsilanes.^{10a,11} For example the 1-silaallene **1**, formed by irradiation of ethynylsilane **2**, underwent an intramolecular addition of the N-H bond to the Si=C bond to form **3**¹² (eq 1).

Transient 1-silaallenes (evidenced by UV spectrometry: π → π* = 275 and 305 nm depending on the substituents^{13,14})



and transition-metal 1-silaallene complexes^{10a,15} have also been reported.

The first stable 1-silaallene, **4** (Ad = adamantyl, Mes* = 2,4,6-tri-*tert*-butylphenyl), was synthesized in 1993 by West:¹⁶ this compound, stabilized by an extremely large steric hindrance around the Si=C=C moiety, was formed by intramolecular addition of a C-Li bond to a C≡C triple bond of alkynylhalosilane **5** followed by elimination of lithium halide (eq 2).



Other stable silaallenes have been synthesized by a slightly different route involving an intermolecular addition of *tert*-butyllithium to a vinylfluorosilane.^{10a,b,17} The reactivity of these silaallenes has been relatively poorly studied. With water and methanol, addition of the O-H bond to the Si=C double bond was observed,^{17a} and a [2 + 2] cycloaddition occurred with benzaldehyde.^{17a} Thermolysis,^{17a} photolysis,^{17b} and reactions with acids¹⁷ resulted in a cyclization of the Si=C double bond with the substituents on the silicon or on the terminal carbon atoms. Silaallenes seem less reactive than silenes, since they are stable for days in the presence of oxygen and moisture at room temperature and react only after heating. This probably is due to the large steric hindrance necessary for their stabilization and, according to calculations, to the less polarized Si=C(sp) double bond.

The thermally stable but photolabile 1-silaallenes **6** were obtained by Sekiguchi¹⁸ by photolysis of silirenes. Compounds **6** finally rearranged to the corresponding alkynylsilanes but were characterized by ¹³C NMR spectroscopy, which displayed

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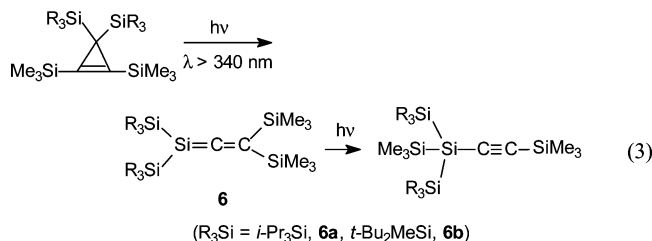
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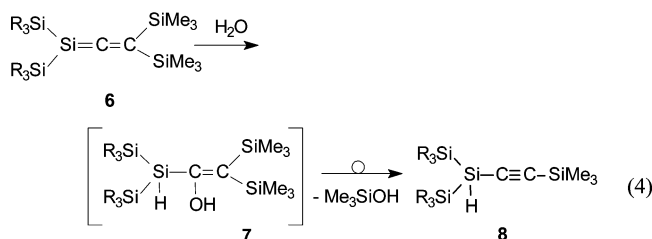
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signals at 268.3 (**6a**) and 267.8 ppm (**6b**) for the central sp carbon atom, and by their ^{29}Si NMR spectra, with signals at -64.2 (**6a**) and -55.0 ppm (**6b**) for the doubly bonded silicon atoms (eq 3). These ^{29}Si NMR chemical shifts are the most



upfield-shifted of $\text{Si}=\text{X}$ double-bonded species, and these assignments have been confirmed by calculations. In 1-silaallenes substituted at silicon by alkyl or aryl groups, ^{29}Si NMR chemical shifts range from 13.1 to 55.1 ppm, depending on the substituents.^{16,17} The marked upfield shift in **6** is due to the electron-donating effect of the trialkylsilyl group on the sp^2 silicon atom, which causes the charge distribution $\text{Si}^{\delta-}=\text{C}^{\delta+}$, in contrast with that of the 1-silaallenes obtained by West, for which a $\text{Si}^{\delta+}=\text{C}^{\delta-}$ polarity was observed.^{10a,b,17} The calculated Mulliken atomic charges on the model compound $(\text{H}_3\text{Si})_2\text{Si}=\text{C}=\text{C}(\text{SiH}_3)_2$ (Si, -0.24 ; sp C, $+0.38$), compared to $+0.09$ and -0.17 , respectively, for $\text{H}_2\text{Si}=\text{C}=\text{CH}_2$, are in good agreement with this reversed polarity of the $\text{Si}-\text{C}$ double bond. This reverse polarity also was confirmed by the reverse addition of water to the $\text{Si}=\text{C}$ double bond of **6**, which when heated with water at 120°C for 24 h gave silylenol **7**,¹⁸ which lost Me_3SiOH to yield the final product **8**. This regiochemistry is opposite to that observed in other $\text{Si}=\text{C}$ double bonds of silenes⁴ and silaallenes^{10a,b,16,17} (eq 4).



Attempts to prepare silabutatrienes have been unsuccessful until now. The formation of the transient silacumulene **9** might be discussed, but detailed studies of this reaction strongly favor the coupling reaction over silacumulene formation¹⁹ (Scheme 1).

In the field of germanium, the sole two 1-germaallenes synthesized thus far, **10**²⁰ and **11**,²¹ were prepared in 1998 by the groups of West and Okazaki/Tokitoh by reaction of *t*-BuLi with a fluorogermylalkyne, as in the case of the 1-silaallene, or by dechlorination by *t*-BuLi of the corresponding dichlorogermapropene (Scheme 2).

The reactivity of germaallenes **10** and **11** toward various reagents has been studied. In all cases, only the $\text{Ge}=\text{C}$ double bond reacted, leading to germylalkenes. Thus, [2 + 1] cycloadditions occurred with sulfur, selenium, and tellurium,²¹ [2 + 2] with benzaldehyde,²⁰ and [2 + 3] with mesitronitrile,²¹ whereas germaallene **10** likely served to hydrate acetone, giving the corresponding vinylgermanol.²⁰ Alcohols and water added to

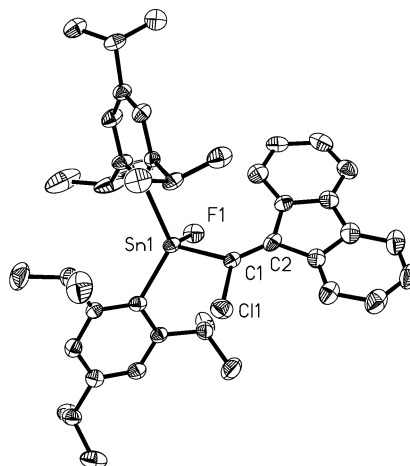


Figure 1. X-ray structure of **12** drawn at the 50% probability level.

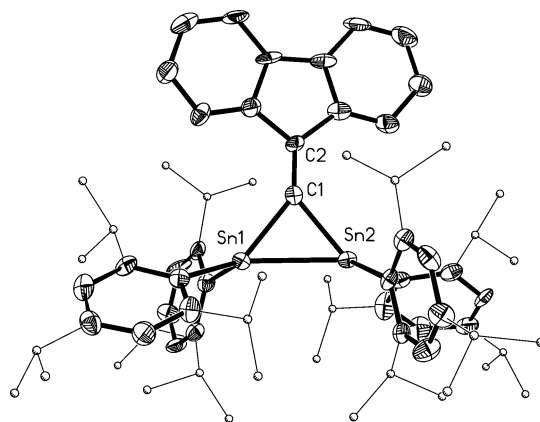


Figure 2. X-ray structure of the distannirane **14** drawn at the 50% probability level.

the $\text{Ge}=\text{C}$ double bond, with oxygen becoming bonded to the germanium atom according to the $\text{Ge}^{\delta+}=\text{C}^{\delta-}$ polarity.^{20,21} By thermolysis, cyclizations of the $\text{Ge}=\text{C}$ double bond with the CH of *i*-Pr²⁰ or of $(\text{Me}_3\text{Si})_2\text{CH}$ ²¹ groups occurred.

Transient 1-Stannaallene $>\text{Sn}=\text{C}=\text{C}<$

As the $\text{Sn}=\text{C}$ double bond is thought to be much more reactive and labile than the $\text{C}=\text{C}$ bond, we have created it in the last step of the synthesis. Thus, the most convenient precursor of the desired stannaallene $>\text{Sn}=\text{C}=\text{C}<$ was the alkenylstannane $>\text{Sn}(\text{X})\text{C}(\text{X}')=\text{C}<$ (X, X' = halogen), which could be dehalogenated by a lithium compound. Such $\text{E}(\text{X})\text{C}(\text{X}')=\text{E}'<$ systems are good precursors for heteroallenes^{10a} (vide infra). In most of the syntheses of doubly bonded main-group elements, the use of fluorine rather than chlorine or bromine as a substituent on the metal atom appeared to be the best solution to avoid side reactions such as reduction of the $\text{E}-\text{Cl}$ (or Br) bond by the lithium compounds. Moreover, the use of fluorine is particularly useful because it allows the monitoring of the reactions by ^{19}F NMR spectroscopy.

The stannylalkene **12**²² was obtained by mixing Tip_2SnF_2 ²³ (Tip = 2,4,6-triisopropylphenyl) and a THF solution of the carbenoid $\text{Li}(\text{Cl})\text{C}=\text{CR}_2$ (CR_2 = fluorenylidene). The latter can be easily prepared by reaction of $\text{Cl}_2\text{C}=\text{CR}_2$ ²⁴ with *n*-butyllithium at low temperature (Scheme 3).

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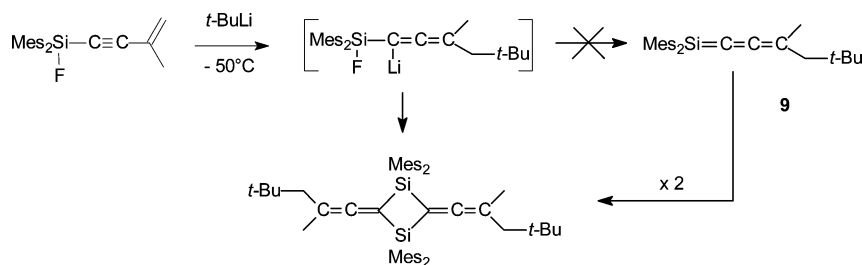
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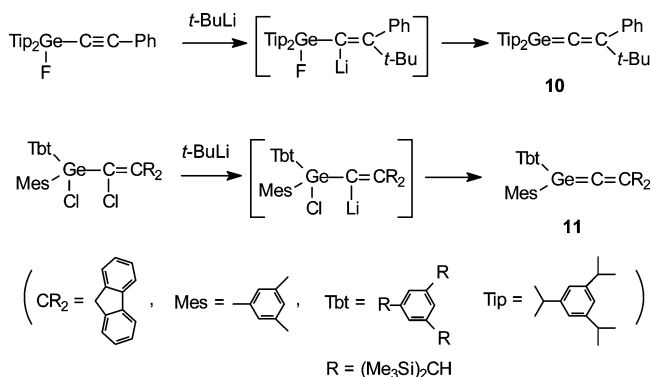
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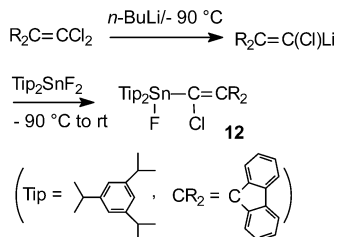
Scheme 1. Attempted Synthesis of a 1-Silabutatriene



Scheme 2. Synthesis of Germaallenes

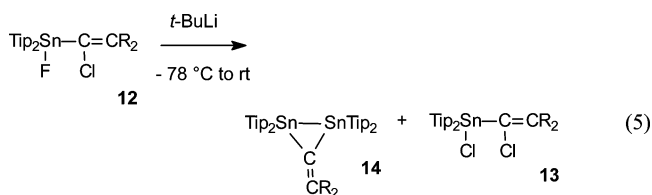


Scheme 3. Synthesis of Stannylalkene 12



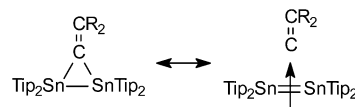
Compound **12** was characterized by mass spectrometry, by NMR spectroscopy, particularly ^{19}F NMR (δ -105.1 ppm, $J_{\text{F}^{117}\text{Sn}} = 2343.9$ Hz, $J_{\text{F}^{119}\text{Sn}} = 2451.3$ Hz) and ^{119}Sn NMR (δ -117.2 ppm), and by its X-ray crystal structure (Figure 1), which showed standard bond lengths (Sn–C = $2.178(4)$ Å, Sn–F = $1.957(3)$ Å, C=C = $1.324(7)$ Å) and bond angles.²²

Surprisingly, addition of 1 equiv of *tert*-butyllithium to a solution of **12** in THF at -78 °C afforded the dichlorostannylalkene **13** (resulting from a F/Cl exchange between **12** and LiCl formed from *t*-BuLi and *t*-BuCl) and 1,1,2,2-tetrakis(2,4,6-triisopropylphenyl)-3-fluorenylidene-1,2-distannirane **14** (eq 5).²² The distannirane **14**, obtained as red crystals, is the first

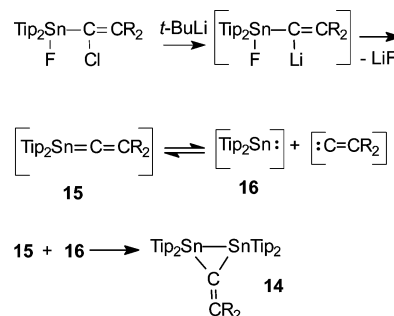


three-membered-ring heterocycle with two tin atoms and one carbon atom. It is surprisingly stable to heat, air, and moisture, despite the high strain of the ring (extremely acute angles on tin and carbon atoms were found in the three-membered ring: $50.7(3)$, $51.3(3)$, and $78.2(4)^\circ$, respectively), probably due to the large steric protection provided by the Tip groups. **14** was characterized by signals at very high field in its ^{119}Sn NMR spectrum (-365.3 ppm), as expected for a three-membered-

Chart 1. Proposed Bonding Situation in Distannirane 14



Scheme 4. Synthesis of Distannirane 14



ring compound, with a large $^1J^{117}\text{Sn}^{119}\text{Sn}$ coupling constant (4673.8 Hz) and by its molecular structure (Figure 2), which deserves some comment. The most intriguing feature is the nearly planar bonding geometry around the tin atoms (as in a SnSnN heterocycle),²⁵ with a shorter Sn–Sn bond ($2.777(2)$ Å) as compared to those in other three- or four-membered tin heterocycles (from 2.827 to 2.889 Å in SnSnTe,²⁶ SnSnSn,²⁷ SnSnC=C,²⁸ and SnSnSS²⁹ rings). Such planar geometry also occurs in three-membered silicon and germanium EEX heterocycles ($E = \text{Si},^{30} \text{Ge};^{31} X = \text{NR}, \text{O}, \text{S}, \text{Se}, \text{Te}$).

Thus, the above results can be interpreted in terms of the Dewar–Chatt–Duncanson model of metal–olefin bonding,³² with bonding intermediate between a π -complex and a standard three-membered-ring derivative (Chart 1).

The formation of **14**²² can be explained by the initial formation of the expected transient stannaallene **15** followed by a [2 + 1] cycloaddition with the stannylene **16** (Scheme 4), since due to the probable lability of the tin–carbon double bond, the stannaallene **15** could behave as a stannylene–carbene complex.

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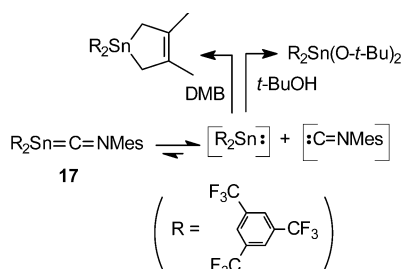
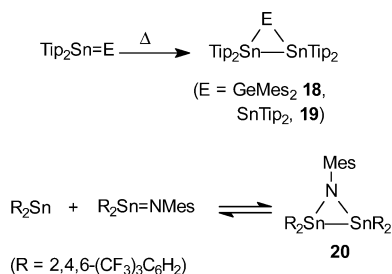
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Scheme 5. Azastannaallene/Stannylene Isocyanide Complex**Scheme 6. From Sn=X to Three-Membered Heterocycles**

Such lability of the Sn=C double bond was observed by Grützmacher in the azastannaallene **17**,³³ which dissociated to a stannylene R₂Sn and an isocyanide (Scheme 5) in reactions with trapping agents, and is explained as a result of the very long Sn–C distance (2.397(3) Å), longer than standard Sn–C single bonds (generally 2.13–2.20 Å³⁴). The strongly bent structure, as predicted by the model of Trinquier and Malrieu,³⁵ and this long Sn–C bond distance show that **17** is better described as a double π-donor–acceptor complex than a formal azastannaallene.³³ A similar bonding probably occurs in stannaallene **15**.

Moreover, formation of three-membered-ring derivatives by [2 + 1] cycloaddition of a stannylene issued from a >Sn=E doubly bonded derivative (E = GeMe₃,³⁶ SnTip₂,³⁷ NMe₃)²⁶ to the as yet intact Sn=E bond to give the corresponding three-membered-ring derivatives **18–20** has already been reported (Scheme 6).

Our results show that a fundamental difference exists in the Sn=C bonding between the stannenes >Sn=C<, with only one tin–carbon double bond, and the stannaallene >Sn=C=C< or azastannaallene >Sn=C=N<,³³ with cumulative tin–carbon and carbon–carbon (or carbon–nitrogen) double bonds, since such behavior of stannenes as a stannylene–carbene complex has generally not been observed. When it is highly sterically hindered, this double bond is stable (cases of **21**³⁸ and **22**³⁹)

(33) Grützmacher, H.; Freitag, S.; Herbst-Irmer, R.; Sheldrick, G. S. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 437.

(34) (a) Charissse, M.; Röller, S.; Dräger, M. *J. Organomet. Chem.* **1992**, *427*, 23. (b) Samuel-Lewis, A.; Smith, P. J.; Aupeas, J. H.; Hampson, D.; Povey, D. C. *J. Organomet. Chem.* **1992**, *437*, 131. (c) Bochkarev, L. N.; Grachev, O. V.; Zillsov, S. F.; Zakharov, L. N.; Struchkov, Y. T. *J. Organomet. Chem.* **1992**, *436*, 299. (d) Cardin, C. J.; Cardin, D. J.; Convery, M. A.; Devereux, M. M. *J. Organomet. Chem.* **1991**, *411*, C3. (e) Weidenbruch, M.; Schäfers, K.; Schlaefke, J.; Peters, K.; Von Schnering, H. G. *J. Organomet. Chem.* **1991**, *415*, 343.

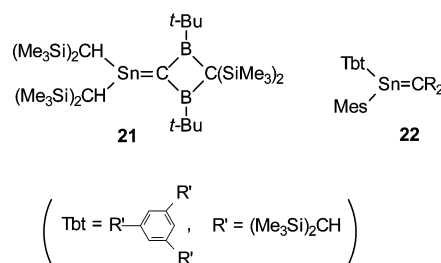
(35) Trinquier, G.; Malrieu, J.-P. *J. Am. Chem. Soc.* **1987**, *109*, 5303.

(36) Chaubon, M. A.; Escudié, J.; Ranaivonjatovo, H.; Satgé, J. *Chem. Commun.* **1996**, 2621.

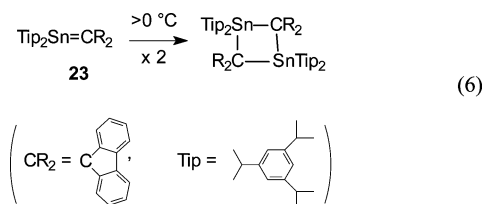
(37) Weidenbruch, M.; Schäfer, A.; Kilian, H.; Pohl, S.; Saak, W.; Marsmann, H. *Chem. Ber.* **1992**, *125*, 563.

(38) (a) Meyer, H.; Baum, G.; Massa, W.; Berger, S.; Berndt, A. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 546. (b) Berndt, A.; Meyer, H.; Baum, G.; Massa, W.; Berger, S. *Pure Appl. Chem.* **1987**, *59*, 1011.

(39) Mizuhata, Y.; Sasamori, T.; Takeda, N.; Tokitoh, N. *Chem. Commun.* **2005**, 5876.

Chart 2. Stable Stannenes

(Chart 2), while a head-to-tail dimer,⁴⁰ formed by cycloaddition of Sn=C double bonds, is observed with **23** with its less bulky groups on Sn and C (eq 6).



Theoretical Studies on >M=C=C< Derivatives. Theoretical studies using standard ab initio and DFT methods were performed by Apeloig et al. on 1-metallaallenes R₂E=C=CH₂ and 2-metallaallenes H₂C=E=CH₂ (E = Si, Ge, Sn, Pb).⁴¹ They predicted that 1-metallaallenes are more stable than 2-metallaallenes for all E elements with a degree of pyramidalization and planarization energies at E and bending at C increasing from Si to Pb. This conclusion was experimentally verified in the case of sila- and germaallenes Tip₂E=C=C(t-Bu)Ph (E = Si, Ge) with a germanium atom more pyramidalized than the silicon atom (sum of angles 348.4°^{17a} versus 357.2°²⁰) and a bending being greater in the germaallene (159.2°²⁰) than in the silaallene (172.0°).^{17a}

According to calculations,⁴¹ while F substitution causes strong pyramidalization at E and a lengthening of the E=C(sp) double bond, SiH₃ substituents on E favor planarization and shorten this double bond. Thus, a bulky silyl group on the tin atom could provide enhanced stabilization for stannaallenes R₂Sn=C=C<.

Phosphaallenes –P=C=C<

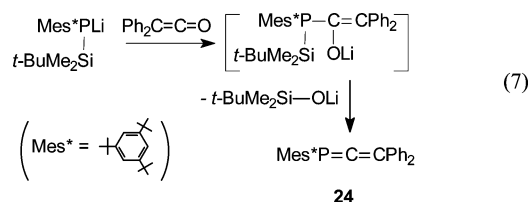
The first heteroallene with one heavier group 15 element to be reported was the phosphaallene **24**,⁴² obtained by Yoshifuji in 1984. Compound **24** was prepared by reaction of diphenylketene with a silyllithiophosphide and was found to be very stable toward heat, light, and atmospheric moisture and oxygen (eq 7). Since 1984, many other phosphaallenes have been synthesized, mainly by the groups of Märkl, Appel and Bickelhaupt.^{10a}

1-Phosphaallenes were obtained by various routes, the most often used being reactions of aldehydes or ketones with a (phosphavinyl)lithium reagent, Wittig reactions between the phosphaketene –P=C=O and phosphoranes, rearrangement of alkynylphosphines in the presence of a base, reaction of a lithium

(40) (a) Anselme, G.; Ranaivonjatovo, H.; Escudié, J.; Couret, C.; Satgé, J. *Organometallics* **1992**, *11*, 2748. (b) Anselme, G.; Declercq, J. P.; Dubourg, A.; Ranaivonjatovo, H.; Escudié, J.; Couret, C. *J. Organomet. Chem.* **1993**, *458*, 49.

(41) Sigal, N.; Apeloig, Y. *Organometallics* **2002**, *21*, 5486.

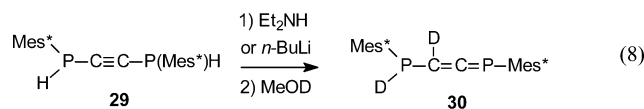
(42) Yoshifuji, M.; Toyota, K.; Shibayama, K.; Inamoto, N. *Tetrahedron Lett.* **1984**, *25*, 1809.



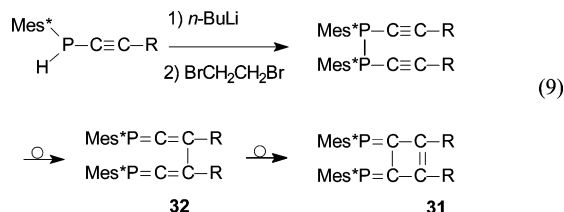
compound with a *C,C*-dichlorophosphirane, and dehydrochlorination of a chlorovinylphosphine. All of these results are described in our previous review.^{10a}

Using some of these routes, new 1-phosphaallenes have been prepared since 2000: transient species such as **25**, which were characterized by trapping with *i*-PrSH,⁴³ and stable examples such as **26**⁴⁴ and **27** or **28**,⁴⁵ prepared by a Peterson-type reaction (Scheme 7).

Alkynylphosphines are especially interesting, since depending on the substituents and on the experimental conditions, they are the precursors of various types of products. For example, phosphallene **30** was obtained from phosphoalkyne **29** by addition of Et₂NH or *n*-BuLi and quenching with MeOD (eq 8).⁴⁶



In the presence of 1,2-dibromoethane, the transient bis(phosphaallenes) **32**⁴⁷ were obtained and rearranged to various 3,4-diphosphinidenecyclobutenes **31**, bearing the supermesityl group (eq 9).



Polymers containing the bis[(2,4,6-tri-*tert*-butylphenyl)phosphinidene]-1,2-bis(2-thienyl)cyclobutene units have also been obtained^{47d} (eq 10).

In the absence of 1,2-dibromoethane, reaction of alkynylphosphines **33** with *n*-BuLi did not afford 3,4-diphosphinidenecyclobutenes **31** but rather 1,4-diphosphafulvenes **34**, which can be regarded as formal dimers of phosphoallenes **36**, probably by a [3 + 2] cycloaddition reaction between 1-phosphaallenes **36** and phosphoallenyl anions **35** formed under the basic conditions⁴⁸ (Scheme 8). This reaction, recently reported

(43) Baba, G.; Tea, C. G.; Touré, S. A.; Lesvier, M.; Denis, J. M. *J. Organomet. Chem.* **2002**, 643–644, 342.

(44) Chentit, M.; Sidorenkova, H.; Choua, S.; Geoffroy, M.; Ellinger, Y.; Bernardinelli, G. *J. Organomet. Chem.* **2001**, 634, 136.

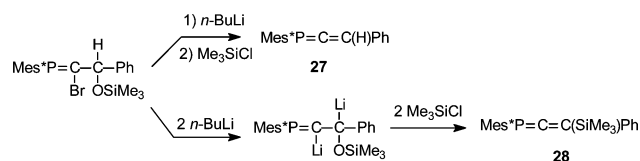
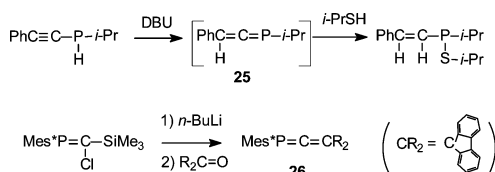
(45) Ito, S.; Sekiguchi, S.; Freytag, M.; Yoshifuji, M. *Bull. Chem. Soc. Jpn.* **2005**, 78, 1142.

(46) Ito, S.; Toyota, K.; Yoshifuji, M. *Heteroat. Chem.* **2000**, 11, 171.

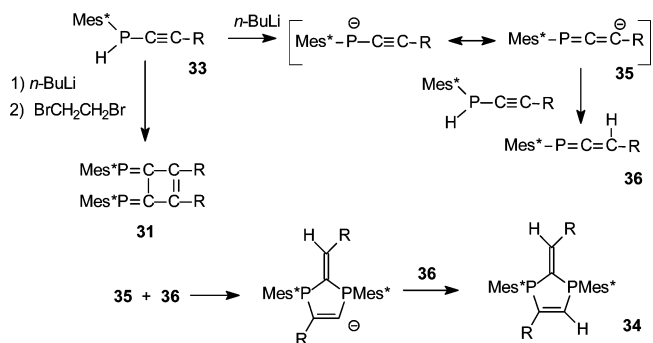
(47) (a) Ito, S.; Freytag, M.; Yoshifuji, M. *Dalton Trans.* **2006**, 710. (b) Yamada, A.; Toyota, K.; Yoshifuji, M. *Org. Lett.* **2002**, 4, 569. (c) Yamada, A.; Toyota, K.; Yoshifuji, M. *Chem. Lett.* **2001**, 248. (d) Toyota, K.; Ujita, J.; Kawasaki, S.; Abe, K.; Yamada, N.; Yoshifuji, M. *Tetrahedron Lett.* **2004**, 45, 7609. (e) Toyota, K.; Abe, K.; Horikawa, K.; Yoshifuji, M. *Bull. Chem. Soc. Jpn.* **2004**, 77, 1377. (f) Ozawa, F.; Yoshifuji, M. *Dalton Trans.* **2006**, 4987.

(48) (a) Ito, S.; Sekiguchi, S.; Freytag, M.; Yoshifuji, M. *J. Org. Chem.* **2004**, 69, 4181. (b) Nakamura, A.; Toyota, K.; Yoshifuji, M. *Tetrahedron* **2005**, 61, 5223.

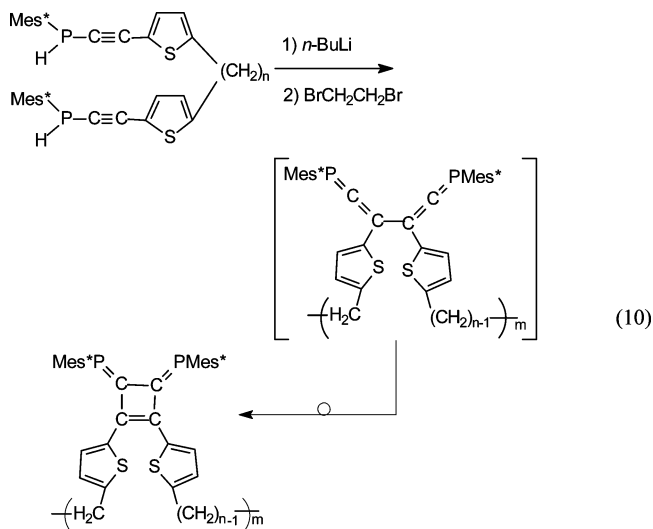
Scheme 7. New Phosphaallenes



Scheme 8. 1,4-Diphosphafulvenes



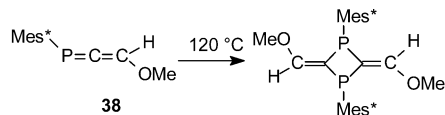
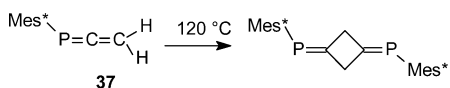
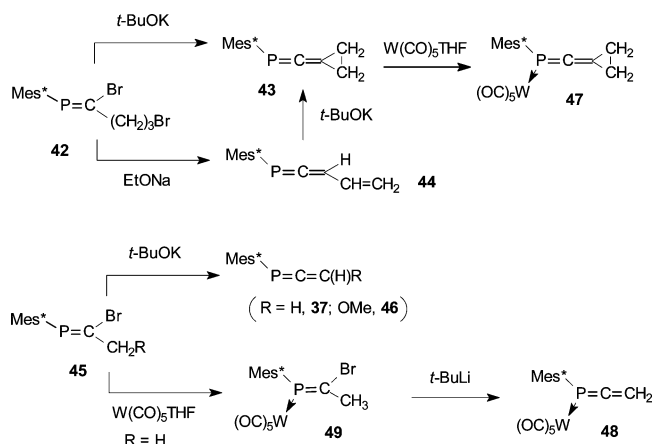
by Yoshifuji, constitutes a novel dimerization pathway of transient 1-phosphaallenes.



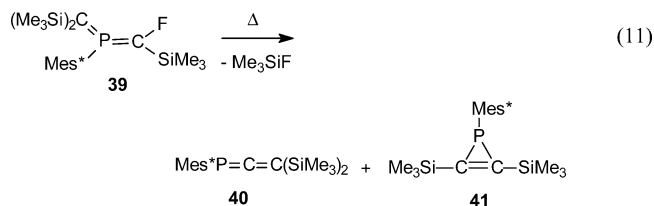
Whereas no dimerization of phosphoallenes **37** and **38** occurred in solution, their thermolysis in the solid state afforded two head-to-tail dimers, by coupling of the C=C bonds of **37** and the P=C bonds of **38**.⁴⁹ The regioselectivity of these dimerizations depends on the substituents at the 3-position, but it is also apparent that the Mes* group controls the arrangement of the molecules in the crystalline state, which steers the regioselectivity of the cycloaddition (Scheme 9).

The mechanism of these topochemical dimerizations of **37** and **38** has not yet been elucidated but could include the generation of radical species, as in the case of phosphabutatrienes.⁵⁰

(49) Ito, S.; Sekiguchi, S.; Yoshifuji, M. *Eur. J. Org. Chem.* **2003**, 4838.

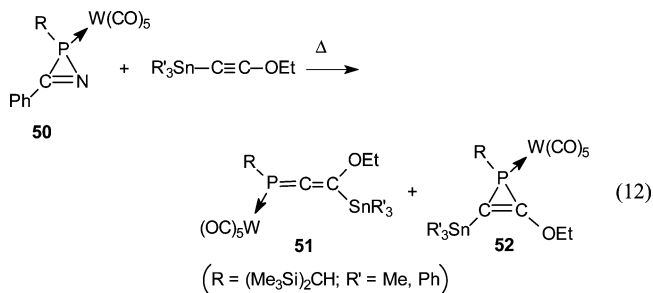
Scheme 9. Dimerization of Phosphaallenes**Scheme 10. New Phosphaallenes and Their η^1 Complexes**

During recent years, other routes allowed the preparation of 1-phosphaallenes. For example, compound **39**, which can be considered as a Si–F–carbenoid, generated phosphaallene **40** and phosphirene **41** in a 1:1 ratio, when heated in refluxing toluene. Although the detailed mechanism could not be determined, this reaction was thought to proceed via α -elimination of Me_3SiF ⁵¹ (eq 11).



Dehydrobromination of phosphaalkene **42** with *t*-BuOK gave phosphaallene **43**. However, with the weaker base EtONa, formation of both **43** and its isomer **44** was observed. The latter gave **43** in the presence of *t*-BuOK through cyclization involving probably 1,2-migration of the allenic proton⁵² (Scheme 10). Similar dehydrobromination of phosphaalkene **45** by *t*-BuOK allowed the synthesis of phosphaallenes **37**^{52b} and **46**.⁴⁹ Unlike **47**, which was obtained by direct complexation of the corresponding phosphaallene **43**, the phosphaallene complex **48** was obtained by dehydrobromination of the starting phosphaalkene complex **49**^{52b} (Scheme 10).

When it was heated with acetylene derivatives, the azaphosphirene tungsten complex **50** gave, among other products, the phosphaallene complex **51**⁵³ and the phosphirene complex **52** (eq 12).



The reactivity of phosphaallenes is very similar to that of phosphaalkenes,⁶ since generally the adjacent C=C double bond does not interfere with the P=C unsaturation, except in the case of the formation of diphosphinidencyclobutenes **31**. Reactions were, for example, observed with protic reagents (addition of the H atom to the central carbon atom according to the $\text{P}^{\delta+}=\text{C}^{\delta-}$ polarity), with sulfur and carbenes to give three-membered-ring derivatives, and with transition-metal complexes with formation of η^1 or η^2 complexes.^{6b,10a}

Phosphaketenes, Phosphathioketenes, and Azaphosphaketenes –P=C=X (X = N, O, S)

The field of phosphaketenes –P=C=O and phosphathioketenes –P=C=S has been practically dormant for the last 5 years, and up to now only *t*-BuP=C=O and $\text{Mes}^*\text{P}=\text{C}=\text{O}$ have been reported,⁵⁴ whereas no phosphathioketene could be characterized by NMR studies.^{10a}

The new stable 1,3-azaphosphaallene $\text{Mes}^*\text{P}=\text{C}=\text{NAr}$ (Ar = *p*-ClC₆H₄) has been synthesized by reaction of a lithium phosphide with the isocyanate ArNCO.^{55a} In contrast to the unsymmetrical dimerization of $\text{Mes}^*\text{P}=\text{C}=\text{NPh}$ catalyzed by Pd(0) complexes,^{55b} YCl₃ catalyzed dimerization by two P=C double bonds to yield the corresponding 1,3-diphosphetane^{55a} (Scheme 11).

The 1,3-azaphosphaallene complex **53** was obtained by coupling of the isocyanide R'NC with the transient terminal phosphinidene complex^{55c} (Scheme 11). Another type of azaphosphaallene complex has been reported, but in contrast to **53**, it is an $\eta^2(\text{N},\text{C})$ titanium complex.^{55d}

The azaphosphaallenide [*i*-PrN=C=P][–]K⁺,^{55e} prepared by reaction of the corresponding aminophosphaalkyne *i*-Pr(Me₃Si)NC≡P with *t*-BuOK, was structurally characterized as its 18-crown-6 ether complex. Quantum chemical calculations and NMR spectroscopic data indicated that the latter lies between the extrema of RN[–]C≡P and RN=C=P[–], suggesting a reactivity typical of an ambident anion. The syntheses, NMR and IR spectroscopic studies, mass spectrometric data, theoretical studies, and reactivities of phosphaketenes, phosphathioketenes, and azaphosphaallenes have been described in a previous review.^{10a}

1-Arsaallenes –As=C=C<

Whereas intensive research has been devoted to doubly bonded derivatives of phosphorus,⁶ fewer studies have been done

(53) Streubel, R.; Wilkens, H.; Ruthe, F.; Jones, P. G. *Z. Anorg. Allg. Chem.* **1999**, 625, 102.

(54) (a) Appel, R.; Paulen, W. *Tetrahedron Lett.* **1983**, 24, 2639. (b) Appel, R.; Siray, M. *Angew. Chem., Int. Ed. Engl.* **1983**, 22, 785.

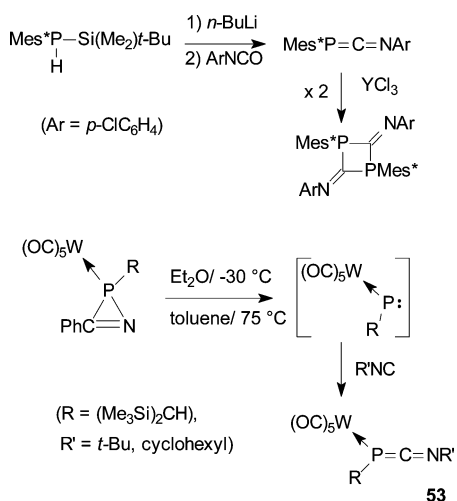
(55) (a) Zhou, X.-G.; Zhang, L.-B.; Cai, R.-F.; Wu, Q.-J.; Weng, L.-H.; Huang, Z.-E. *J. Organomet. Chem.* **2000**, 604, 260. (b) David, M. A.; Alexander, J. B.; Glueck, D. S.; Yap, G. P. A.; Liabe-Sands, L. M.; Rheingold, A. L. *Organometallics* **1997**, 16, 378. (c) Ionescu, E.; Von Frantzius, G.; Jones, P. G.; Streubel, R. *Organometallics* **2005**, 24, 2237. (d) Basuli, F.; Watson, L. A.; Huffman, J. C.; Mindiola, D. J. *Dalton Trans.* **2003**, 4228. (e) Becker, G.; Brombach, H.; Horner, S. T.; Niecke, E.; Schwarz, W.; Streubel, R.; Würthwein, E.-U. *Inorg. Chem.* **2005**, 44, 3080.

(10) (a) Märkl, G.; Kreitmeyer, P. *Tetrahedron Lett.* **1989**, 30, 3939. (b) Märkl, G.; Kreitmeyer, P.; Nöth, H.; Polborn, K. *Tetrahedron Lett.* **1990**, 31, 4429. (c) Schoeller, W. W.; Welz, U.; Haug, W.; Busch, T. *Chem. Ber.* **1991**, 124, 271.

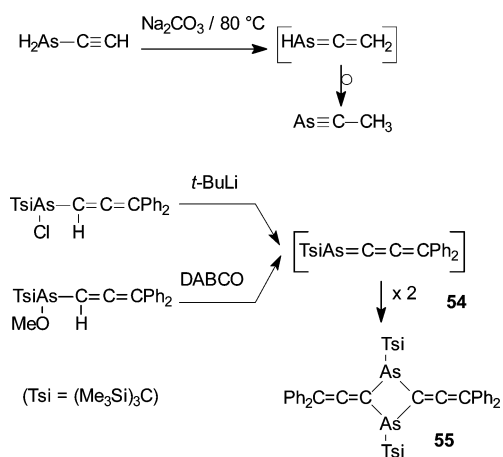
(51) Baumgartner, T.; Moors, P.; Nieger, M.; Hupfer, H.; Niecke, E. *Organometallics* **2002**, 21, 4919.

(52) (a) Ito, S.; Kimura, S.; Yoshifuji, M. *Org. Lett.* **2003**, 5, 1111. (b) Ito, S.; Kimura, S.; Yoshifuji, M. *Bull. Chem. Soc. Jpn.* **2003**, 76, 405.

Scheme 11. 1,3-Azaphosphaallenes



Scheme 12. Transient Arsaallene and Arsabutatriene



on their arsenic analogues.⁷ This is due to many factors, particularly to the lack of convenient arsenic NMR. This requires the isolation of pure compounds for their identification, whereas ³¹P NMR spectroscopy is a powerful tool that allows the determination of the solution structures of organophosphorus compounds, even in complex mixtures. The toxicity of some arsenic compounds and the supposition that the stabilization of multiply bonded arsenic derivatives should be more difficult than of the phosphorus analogues have discouraged many researchers, although arsaalkenes have proven to be isolable.⁷

By analogy with phosphorus,^{56a} the transient arsaallene HAs=C=CH₂ was postulated as a possible intermediate in the rearrangement of an alkynylarsane on sodium carbonate to give an arsaalkyne^{56b} (Scheme 12).

A compound with three cumulative double bonds, the arsabutatriene **54**, was also postulated as a possible intermediate in the dehydrohalogenation or dehydromethoxylation of an arsanallene, giving the 1,3-diarsetane **55**^{56c} (Scheme 12).

The sole arsaallene complexes were obtained by treatment of a tungsten complex with an equimolar amount of the arsaalkene R'As=C(NMe₂)₂. The mechanism of their formation probably involves the initial nucleophilic attack of

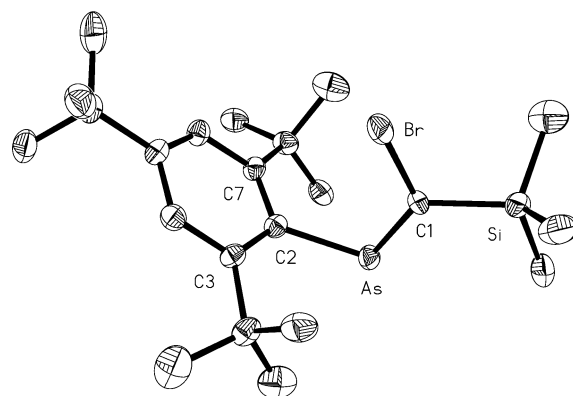
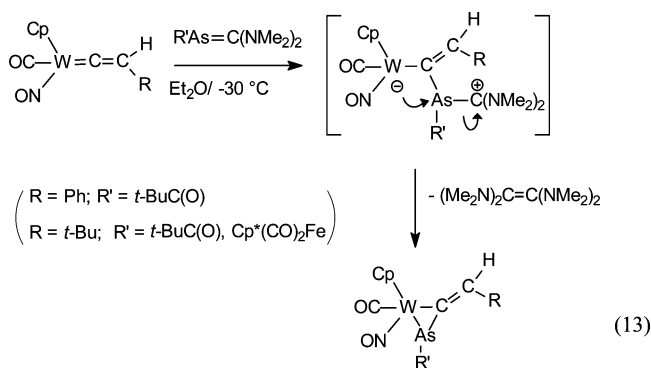


Figure 3. X-ray structure of the arsaalkene **59** drawn at the 50% probability level.

arsaalkenes by their As atom on the C atom bonded to the tungsten, followed by ring closure and extrusion of the carbene C(NMe₂)₂ (eq 13).^{56d}



In order to synthesize stable arsaallene derivatives -As=C=C<, it seemed possible to create in the first step either the carbon-carbon or the arsenic-carbon double bond, since the arsaalkenes -As=C< substituted on arsenic by bulky groups appeared to be rather well stable.⁷ The first formation of the As=C double bond involved the preparation of *C,C*-dihaloarsaalkenes -As=CX₂⁵⁷ (X = Cl, **56**; X = Br, **57**; X = I, **58**), the arsenic analogues of the *C,C*-dihalo phosphoalkenes -P=CX₂,⁵⁸ which have proven to be very important building blocks in phosphorus chemistry.

As expected, compounds **56–58**, easily synthesized from Mes*AsF₂,⁵⁹ are very useful for the preparation of functionalized arsaalkenes by halogen-metal exchange with *n*-butyllithium. For example, the *C*-bromo-*C*-(trimethylsilyl)arsaalkene **59** was easily prepared in a two-step procedure.⁶⁰ As in the case of its phosphorus analogue, the *Z* isomer was obtained (see Figure 3 for the solid-state structure), in agreement with the expected mechanism involving Li/Br exchange from the less hindered side. Subsequent addition to **59** of *n*-butyllithium that was then followed by fluorenone addition (in order to include the carbon atom into the fluorenylidene group chosen for its ability to favor crystallization and to stabilize doubly bonded compounds) led,

(57) Randane, H.; Ranaivonjatovo, H.; Escudié, J.; Knouzi, N. *Organometallics* **1996**, *15*, 2683.

(58) (a) Goede, S. J.; Bickelhaupt, F. *Chem. Ber.* **1991**, *124*, 2677. (b) Van der Sluis, M.; Wit, J. B.; Bickelhaupt, F. *Organometallics* **1996**, *15*, 174.

(59) Cowley, A. H.; Kilduff, J. E.; Lasch, J. G.; Mehrotra, S. K.; Norman, N. C.; Pakulski, M.; Whittlesey, B. R.; Atwood, J. L.; Hunter, W. E. *Inorg. Chem.* **1984**, *23*, 2582.

(60) Bouslikhane, M.; Gornitzka, H.; Ranaivonjatovo, H.; Escudié, J. *Organometallics* **2002**, *21*, 1531.

(56) (a) Guillemin, J. C.; Janati, T.; Denis, J. M. *J. Chem. Soc., Chem. Commun.* **1992**, 415. (b) Guillemin, J.-C.; Lassalle, L.; Drean, P.; Włodarczyk, G.; Demaison, J. *J. Am. Chem. Soc.* **1994**, *116*, 8930. (c) Märkl, G.; Reithinger, S. *Tetrahedron Lett.* **1990**, *31*, 6331. (d) Weber, L.; Bayer, P.; Noveski, G.; Stammner, H.-G.; Neumann, B. *Eur. J. Inorg. Chem.* **2006**, 2299.

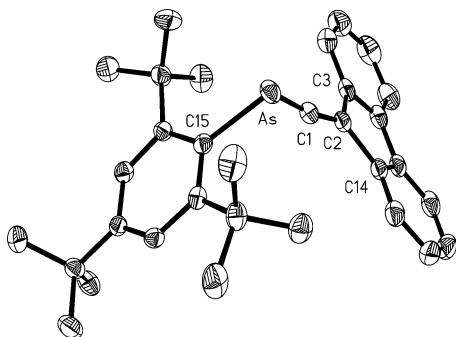
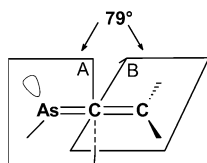
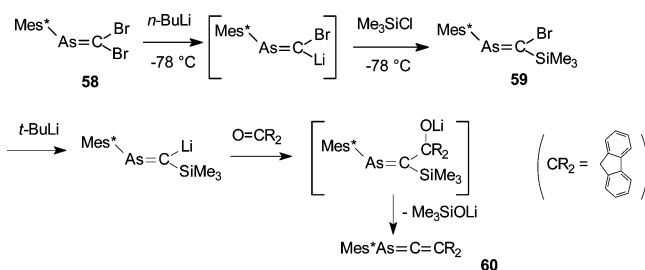


Figure 4. X-ray structure of the arsaallene **60** drawn at the 50% probability level.

Chart 3. Dihedral Angle in the $-\text{As}=\text{C}=\text{C}<$ Species **60**



Scheme 13. Stable Arsaallene **60**



by a Peterson elimination of Me_3SiOLi at room temperature, to the expected arsaallene **60**⁶⁰ in nearly quantitative yield (Scheme 13).

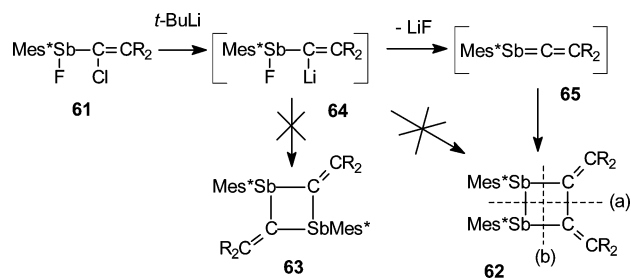
The arsaallene **60** is remarkably stable toward air and moisture. Colorless crystals of **60** were recovered unchanged after some days in air at room temperature. It exhibits characteristic ^{13}C NMR resonances for the sp carbon atom with a chemical shift at very low field (δ 255.8 ppm) (comparable to 233.44 ppm for $\text{Mes}^*\text{P}=\text{C}=\text{CR}_2$ ⁴⁴ or 237.6 ppm for $\text{Mes}^*\text{P}=\text{C}=\text{CPh}_2$ ⁴² and more generally 233–250 ppm for $-\text{P}=\text{C}=\text{C}<$ ^{10a}) and for the terminal carbon atom at 129.1 ppm (128.1 and 128.3 ppm in $\text{Mes}^*\text{P}=\text{C}=\text{CR}_2$ ⁴⁴ and $\text{Mes}^*\text{P}=\text{C}=\text{CPh}_2$ ⁴² respectively).

Interesting features are observed in the structure of **60**,⁶⁰ as obtained by X-ray crystallography (Figure 4). Its bonding system is rather close to the ideal allenic structure: the AsCC bond angle ($169.7(2)^\circ$) and the angle between the planes A and B (79.3°) (Chart 3) are not too far from 180 and 90° , respectively. **60** has a particularly short As=C bond length ($1.754(2)$ Å), corresponding to a shortening of about 10–12% in comparison with standard As–C single-bond lengths (generally 1.97 – 2.00 Å⁷). The As=C bond in **60** is slightly shorter than the As=C distance determined in its precursor **59** ($1.789(3)$ Å⁶⁰). However, the shortening of 0.035 Å is probably partly due to the smaller bond radius of the sp-hybridized carbon atom in **60**.

Transient Stibaallene $-\text{Sb}=\text{C}=\text{C}<$

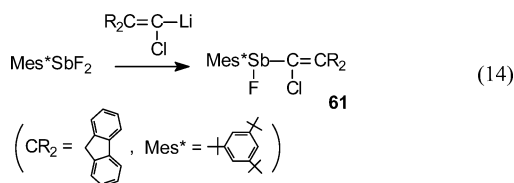
In order to compare the stability of stibaallenes $-\text{Sb}=\text{C}=\text{C}<$ with that of their phosphorus⁴⁴ and arsenic⁶⁰ analogues, we

Scheme 14. Transient Stibaallene **65**



planned to prepare $\text{Mes}^*\text{Sb}=\text{C}=\text{CR}_2$ ⁶¹ with the same supermesityl group on antimony and including the terminal carbon atom in the fluorenylidene group. Arsaallene **60** was prepared by a route involving the initial formation of the As=C double bond, which was successful, owing to the good stability of this bond. However, Sb=C double bonds are much less stable⁸ and only a few stibaalkenes $-\text{Sb}=\text{C}<$ have been characterized, such as $\text{R}(\text{O})\text{CSb}=\text{C}(\text{OH})\text{R}$ ($\text{R} = t\text{-Bu, Mes, Mes}^*$)⁶² and $2\text{-Pyr}(\text{Me}_3\text{Si})_2\text{CSb}=\text{C}(\text{SiMe}_3)_2$ ($\text{Pyr} = \text{C}_5\text{H}_5\text{N}$),⁶³ along with the two 2,3-distibabutadienes $\text{R}'(\text{Me}_3\text{SiO})\text{C}=\text{SbSb}=\text{C}(\text{OSiMe}_3)\text{R}'$ ($\text{R}' = \text{Mes, Mes}^*$).⁶⁴

Thus, a different synthetic strategy was followed involving initial creation of the C=C double bond and formation of the Sb=C unsaturation in the final step. Stibapropene **61**⁶¹ was obtained by reaction of the carbenoid $\text{R}_2\text{C}=\text{C}(\text{Li})\text{Cl}$ with the stibane Mes^*SbF_2 (eq 14).



Addition of *tert*-butyllithium to a THF solution of **61** at -90 °C afforded the 1,2-distibacyclobutane **62**⁶¹ (Scheme 14). Whereas the 1,3-distibacyclobutane **63** could result from the coupling of two molecules of the intermediate lithium compound **64**, the formation of **62** could be explained, for electric charge reasons, only by the head-to-head dimerization of the transient stibaallene **65**.⁶¹ Similar head-to-head dimerization has been reported for allenes with a terminal fluorenylidene group such as $\text{R}_2\text{C}=\text{C}=\text{C}(\text{Ph})\text{Cl}$, leading to the corresponding 1,2-bis(9-fluorenylidene)cyclobutane;⁶⁵ one of the driving forces for this head-to-head dimerization probably is the possibility of conjugation in the $\text{R}_2\text{C}=\text{C}=\text{C}=\text{CR}_2$ moiety.

Although satisfactory single crystals could not be obtained for an X-ray structural analysis, the structure of **62** was unambiguously assigned on the basis of chemical ionization (NH_3) mass spectrometry with the presence of a protonated

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Table 1. PM3 Calculated Enthalpies (kcal mol⁻¹) of **62**, **63**, and **65**

	$\Delta H(\text{dimer}) - 2[\Delta H(\text{monomer})]$	cis-trans rel energies
65	0	
cis- 62	-78.475	+4.828
trans- 62	-83.403	0.0
cis- 63	-48.731	+8.520
trans- 63	-57.251	0.0

Table 2. Dimerization Energies (kcal mol⁻¹) of the Model Compounds

	RHF/gen	B3LYP/lanl2dz(dp)
65H	0	
cis- 62H	-79.75	-65.51
trans- 62H	-83.08	-68.56
cis- 63H	-57.39	-49.71
trans- 63H	-57.12	-49.71

molecular peak at *m/z* 1007, by the fragmentation pattern (fragments corresponding to Mes^{*}Sb=C=CR₂ and R₂C=C=C=CR₂ due to cleavage according to (a) and (b) in Scheme 14, respectively), and by its ¹H and ¹³C NMR spectra.

Molecular orbital calculations at the PM3 level performed on Mes^{*}Sb=C=CR₂ (**65**) show a great stabilization of the dimer in relation to the monomer. Among all of the possible isomers, the head-to-head dimer is more favored than the head-to-tail one and in both cases the trans isomer is lower in energy, as expected from steric hindrance considerations⁶¹ (Table 1).

With more sophisticated methods (ab initio and DFT) performed on hydrogen-substituted derivatives **65H**, **62H**, and **63H**, similar results were obtained⁶¹ (Table 2).

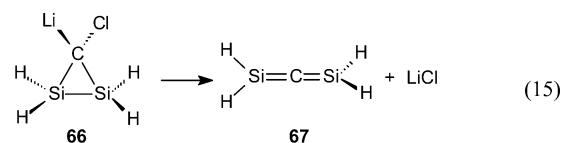
Whereas the four-membered ring in **63H** is predicted to be planar, with the two C=CH₂ moieties in the plane, it is bent along the Sb...C axis in **62H** with the two C=CH₂ moieties twisted by 42.58° (RHF calculations). However, the dienic conjugation between the two C=CH₂ moieties seems to be partially maintained, since the central C-C bond (1.487 Å) is shorter than a standard C-C single bond.

According to the examination of frontier orbitals of **65H**, the HOMO and LUMO (-0.8000 and 1.497 eV, respectively)⁶¹ are composed mainly of antimony 5p and central carbon 2p orbitals. As the contributions from Sb are greater, it is expected that the Sb-Sb bond is formed in the first step of the dimerization. Thus, calculations support the experimental data of the head-to-head dimerization of stibaallene **65**, with probably the formation of the trans isomer.

Dimetallaallenes >E₁₄=C=E₁₄<

No experimental work on transient or stable dimetallaallenes of the type E₁₄=C=E₁₄ (E₁₄ = Si, Ge, Sn) has been reported to date. Whether disilacyclopropylidenes and their carbenoids are appropriate precursors for the unknown 1,3-disilaallenes was examined by means of ab initio molecular orbital calculations.⁶⁶ The computational study of the potential energy surface for the elimination of LiCl from the parent cyclo-CSi₂H₄CLi (**66**) predicted that the conversion of carbenoid **66** to the parent 1,3-disilaallene **67** (+LiCl) corresponds to only 6.5 kcal mol⁻¹ in activation energy and a free-energy difference Δ*G* (at *T* = 298 K) of -13.4 kcal mol⁻¹ (eq 15).

The reaction should proceed without the intermediacy of the corresponding 1,2-disilacyclopropylidene, which appears not to be a minimum on the potential energy surface. A successful synthesis of 1,3-disilaallenes by this route requires the efficient removal of LiCl from the reaction medium to circumvent the



spontaneous and exothermic addition of LiCl (Δ*H* = -40.3 kcal mol⁻¹) across the Si=C double bond.

The parent 1,3-disilaallene **67** adopts a classical allenic-type structure with *D*_{2d} symmetry. The Si=C bond length of 1.692 Å in disilaallene **67**⁶⁶ matches previous computational (1.702⁶⁷ and 1.703 Å⁶⁸) and experimental findings (1.704(4)¹⁶ and 1.693(3) Å^{17a}) for 1-silaallenes.

1,3-Phosphametallaallenes -P=C=E₁₄<

Unlike the 1,3-dimetallaallenes >E₁₄=C=E₁₄<, their phosphorus counterparts, 1,3-phosphametallaallenes -P=C=E₁₄<, have been experimentally investigated.⁶⁹

A general approach to such heteroallenes consists in dehalogenation of the corresponding 2,3-dihalopropenes **I** (Scheme 15). The preferred dihalogenated precursors **I** feature a P=C double bond because of their higher thermodynamic stability and lower reactivity compared to those of E₁₄=C double-bond-containing compounds. They are obtained according to the Bickelhaupt procedure⁵⁸ by successive lithiation of the starting dihalophosphaalkenes Mes^{*}P=CX₂ (X = Cl, Br) and coupling of the thus generated carbenoids Mes^{*}P=CXLi with halosilanes or germanes. The more accessible *E*-halogen atom in Mes^{*}P=CX₂ is replaced by a silyl or germyl group in the course of this reaction sequence. Dehalogenation of these vicinal dihaloheteropropenes **I** is initiated by lithium/halogen exchange by treatment with an alkylolithium. The intermediate phosphoenyllithium derivatives **II** give rise to ³¹P NMR signals shifted to lower field and proceed with elimination of lithium halide, generating the E₁₄=C double bond adjacent to the starting P=C bond.

Sterically demanding substituents attached to both hetero-elements serve to increase the stability of the target heteroallenes by retarding or preventing their dimerization.

Applying the method described above using Mes^{*}P=CCLi₂ (Mes^{*} = 2,4,6-*tert*-butylphenyl) and TipPhSiCl₂ (Tip = 2,4,6-triisopropylphenyl) as starting materials successfully provided the first phosphasilaallene Mes^{*}P=C=SiTipPh (**68**).^{69a} The (chlorophosphasilapropenyl)lithium **69** (δ(³¹P) 417.6 ppm) was formed by adding *tert*-butyllithium to Mes^{*}P=C(Cl)Si(Cl)TipPh at -80 °C. It decomposed at -60 °C, giving phosphasilaallene **68** as the major product in 60% yield (Scheme 16).

In the absence of a trapping reagent, phosphasilaallene **68** dimerized above -20 °C.

In contrast to the case for **69**, the analogous Mes^{*}P=C(Li)-SiCl₂R (**70**; R = 9-methylfluoren-9-yl) did not undergo LiCl elimination, even when the solution was heated for a long time.⁷⁰ This method failed to yield the desired 3-chlorophosphasilaallene **71**, which would have been a valuable building block with the

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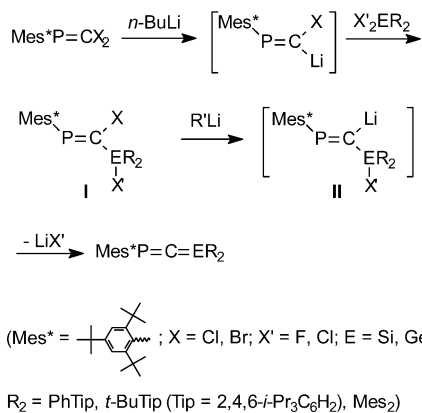
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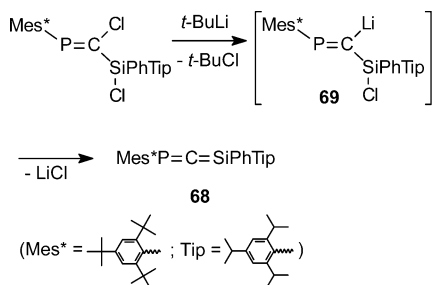
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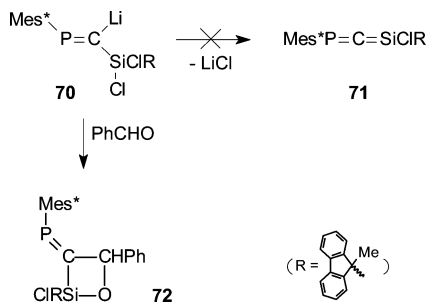
Scheme 15. General Preparation of 1,3-Phosphametalloallenes



Scheme 16. Synthesis of Mes*P=C=SiTipPh (68)

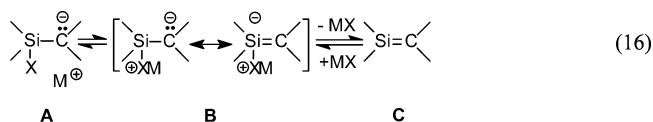


Scheme 17. Chemical Behavior of Mes*P=C(Li)SiCl2R (70)



added reaction site supplied by the Si–Cl bond (Scheme 17). The surprising stability of compound **70** and its reluctance to lose lithium halide were explained by theoretical studies at the RHF/3-21G* and RHF/6-31G**//RHF 3-21G* levels. The lowest-energy conformer of the model Mes*P=C(Li)SiCl₂Cp' (Cp' = 1-methylcyclopentadienyl) exhibits strong electronic interactions between Li and both π -systems, as supported by the following distances: Li–*ipso*-C(Mes*) = 2.357 Å, Li–centroid(Mes*) = 2.380 Å, Li–*ipso*-C(Cp') = 2.325 Å, and Li–centroid(Cp') = 2.247 Å. Similar interactions were observed by X-ray diffraction analysis of the lithium (difluorosilyl)-phosphide RF₂Si–P(Li)SiMe₃ (R = 2,6-dimesitylphenyl), which failed to eliminate lithium fluoride up to 100 °C.⁷¹ Moreover, calculations on the natural charges in model carbanions (HP=C(SiH_xCl_{3-x})⁻ at the RHF/6-31+G** level show increasing negative charge on the carbon atom with an increasing number of chlorine atoms on silicon. Both results favor the **A** form proposed by Wiberg for 1,2-elimination of LiX to form a Si=C double bond (eq 16).⁷²

The reaction of Mes*P=C(Li)SiCl₂R (**70**) with benzaldehyde gives the oxasiletane **72**, which should also be obtained by a [2



+ 2] cycloaddition between benzaldehyde and the Si=C double bond of the corresponding chlorophosphasilaallene **71** (Scheme 17). A similar [2 + 2] cycloaddition, without participation of the contiguous P=C double bond, was found for the Ge congener Mes*P=C=GeTip(*t*-Bu)^{69c} (eq 18).

The method described in Scheme 15 provided the way to the synthesis of the first phosphagermaallene, Mes*P=C=GeMes₂ (**73**).^{69b} Dehalogenation of the 2,3-bromofluoro-1,3-phosphagermapropene **74** was carried out with *n*-butyllithium at –90 °C. The stronger fluorine–germanium bond slows down side reactions such as alkylation of the germanium atom or reduction of the germanium–halogen bond. Loss of LiF from the ((fluorogermyl)phosphaalkenyl)lithium species **75** with formation of the Ge=C double bond took place at –60 °C, affording the anticipated phosphagermaallene **73**. Seventy percent of the reaction product, according to ³¹P NMR analysis, was compound **73**. Above –30 °C phosphagermaallene **73** dimerized (Scheme 18).

Obviously, stabilization of the P=C=Ge framework requires a greater steric shielding. This was achieved by having the bulkier Tip and *tert*-butyl groups on the germanium atom. The 1,3-phosphagermaallene Mes*P=C=GeTip(*t*-Bu) (**76**), the first stable heteroallene that contains two heavier double-bonded group 14 and 15 elements, was obtained quantitatively as an orange solid by the usual dehalogenation of dihalophosphagermapropene **77** with *tert*-butyllithium at –80 °C (Scheme 19).^{69c}

Physical Properties. ¹³C NMR spectroscopy was a useful diagnostic tool for establishing the structure of 1,3-phosphametalloallenes. Phosphasilaallene **68** and phosphagermaallenes **73** and **76** exhibit typical ¹³C chemical shifts for the sp²-hybridized carbon atom at 269.1 (d, ¹J_{CP} = 45.8 Hz),^{69a} 280.9 (d, ¹J_{CP} = 54.3 Hz),^{69b} and 280.8 ppm (d, ¹J_{CP} = 62.1 Hz),^{69c} respectively. Comparable data ranging from 209 to 277 ppm^{10a} have been reported for heteroallenes such as 1-silaallenes, 1-germaallenes, 1-phosphaallenes, and 1,3-diphosphaallenes. Heteroallenes **68**, **73**, and **76** also were characterized by similar low-field chemical shifts in their ³¹P NMR spectra (288.7,^{69a} 239.7,^{69b} and 249.9 ppm,^{69c} respectively), in the region expected for such phosphorus derivatives incorporating E₁₄ elements of lower electronegativity (Figure 5).^{10a}

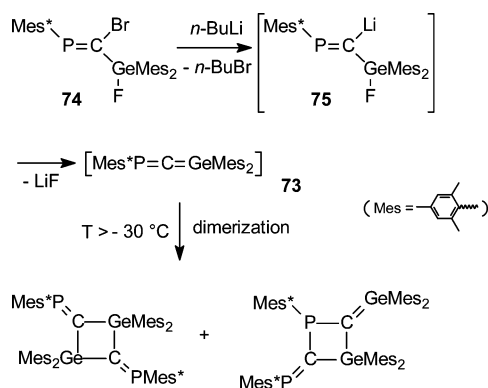
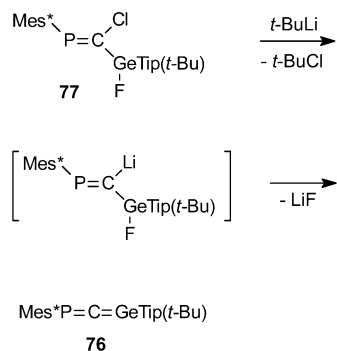
The ²⁹Si chemical shift of phosphasilaallene **68** (75.7 ppm)^{69a} also confirms the presence of a Si=C double bond, as found for silaalkenes⁴ and silaallenes,^{16,17} and clearly differs from those of silylene–isocyanide complexes (–48 to –58 ppm) (see Charts 5 and 6 and ref 74).

Reactivity. As mentioned previously, phosphasilaallene **68** and phosphagermaallene **73** readily dimerized when the reaction mixtures were warmed to room temperature.^{69a,b} Dimerization reactions followed two different pathways involving either P=C and E₁₄=C (E₁₄ = Si, Ge) double bonds or two E₁₄=C double bonds (Scheme 20).

The major dimers 1,3-phosphasila(or germa-)cyclobutanes derived from the [P=C + E=C] mode likely feature the exocyclic P=C bond with the Mes* group and the intracyclic phosphorus atom in anti disposition, as could be deduced from the extent of the coupling constant ²J_{PP}. The latter pathway led to minor dimers 1,3-disila(or germa-)cyclobutanes in the form of a sole trans (along the P=C⋯C=P axis) isomer. Cis–trans isomerization took place gradually at room temperature or more

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Scheme 18. Synthesis of Mes*P=C=GeMes₂ (73)Scheme 19. Synthesis of Mes*P=C=GeTip(*t*-Bu) (76)

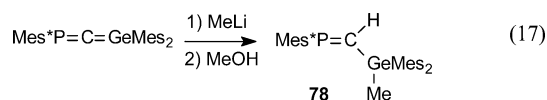
rapidly upon UV irradiation to reach an equilibrium between both isomers. The selective formation of 1,3-disilacyclobutane featuring two Tip groups on the same side of the four-membered ring, as shown by an X-ray structure determination, favored a concerted [2 + 2] cycloaddition of two Si=C double bonds.^{69a}

Other heteroallenes such as ketenes⁷³ and azaphosphaallenes –P=C=N–^{55a,b} also dimerize by two analogous routes.

The relative energies of the dimers of the parent HP=C=GeH₂ have been determined by restricted Hartree–Fock calculations^{69b} and are shown in Chart 4. Only a small difference was found between head-to-head and head-to-tail arrangements for each pair of dimers. The butterfly structures were predicted to be the most stable but were not formed, probably because of the large size of the substituents used. This also accounted for discrepancies between experimental and theoretical results.

Water and methanol added chemoselectively across the E=C bond of the P=C=E systems with the proton bonded to the negatively charged carbon. The P=C unit remained intact, even when an excess of the reagent was used (Scheme 21).⁶⁹

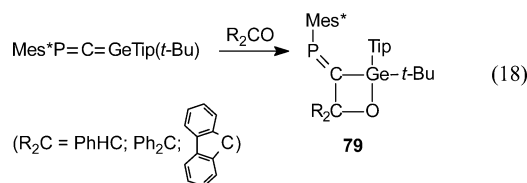
Attack at the more positive germanium atom by nucleophiles such as methylolithium and subsequent quenching with methanol gave the gemylphosphaalkene **78** (eq 17).^{69b}



[2 + 2] cycloaddition reactions were observed with Mes*P=C=GeTip(*t*-Bu) and benzaldehyde, benzophenone, and fluorenone to afford the oxagermetanes **79**, which feature an exocyclic (Z)-P=C double bond (eq 18).

Whereas the PCE sequences (E = Si, Ge) are maintained in the above reactions, a striking difference is observed with their

azasilaallenes **80**^{74a–f} and azastannaallene **17**³³ analogues (Chart 5), since the latter dissociate in solution into isocyanides and silylenes and stannylene, respectively. Only the reaction products of the silylenes or stannylene were obtained.



Thus, azasilaallenes **80** and azastannaallene **17** could be described as complexes of silylenes (or stannylenes) and isocyanides (Chart 6). In the case of the novel azasilaallenes **81**,^{74g} some characteristics (CNC bond angles in the range 130.69–146.3°, narrower than 180°, which indicate close to sp²-hybridized N atoms and the ²⁹Si resonances at lower field (15.9 and 23.9 vs –48 to –58 ppm in **80**)), suggest a heteroallene structure for this derivative.

1,3-Diphosphaallenes

Among neutral heteroallenes incorporating a trivalent phosphorus atom and featuring the P=C=P sequence (Chart 7), the 1σ²,3σ²-diphosphaallenes **III**⁷⁵ and their η¹ transition-metal complexes **IV**⁷⁶ have been known for many years.^{6,10a} More recently 1σ⁴,3σ²-diphosphaallenes **V** have been isolated.⁷⁷ We recently have been successful in the preparation of another class of diphosphaallenes, 1σ³,3σ²-diphosphaallenes **VI**.⁷⁸

1σ²,3σ²-Diphosphaallenes. The preparation of stable 1σ²,3σ²-diphosphaallenes can be achieved by starting from differently substituted 1,3-diphosphapropenes by HX abstraction with bases,^{75b,79} dehalogenation,⁸⁰ lithium silanolate elimination,^{75a,b} or photochemical extrusion of carbon disulfide.⁸¹ Peterson olefination-like reactions involving a phosphaketene^{75a} or

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(81) Appel, R.; Fölling, P.; Krieger, L.; Siray, M.; Knoch, F. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 970.

(73) Tenud, L.; Weilemann, M.; Dallwigk, E. *Helv. Chim. Acta* **1977**, *100*, 975.

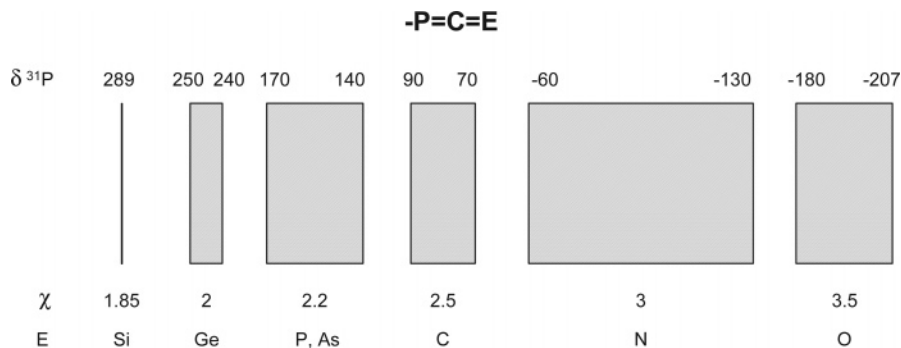


Figure 5. Variation of ^{31}P chemical shifts in $-\text{P}=\text{C}=\text{E}$ with electronegativity.

Scheme 20. Dimerization Pathways of 1,3-Phosphametalloallenes 68 and 73

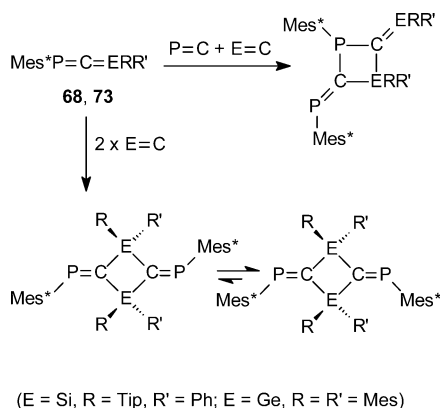
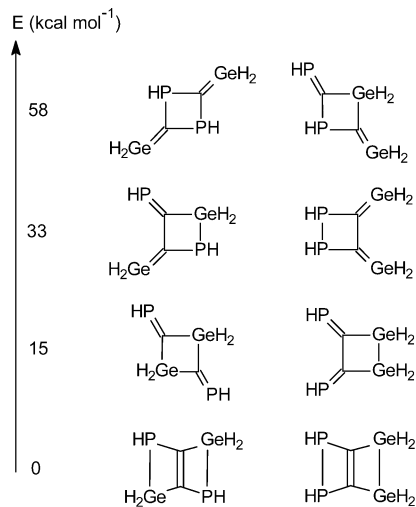


Chart 4. Relative Energies of Dimers of the Parent Phosphagermaallene $\text{HP}=\text{C}=\text{GeH}_2$



intermediate phosphathioketene⁸² and ring-opening reactions of functionalized diphosphiranes^{80,83} also have provided stable $1\sigma^2,3\sigma^2$ -diphosphaallenes (Scheme 22). All of the isolated

(82) (a) Krieger, L. Ph.D. Dissertation, University of Bonn, Bonn, Germany, 1988. (b) Chentit, M.; Sidorenkova, H.; Jouaiti, A.; Terron, G.; Geoffroy, M.; Ellinger, Y. *J. Chem. Soc., Perkin Trans. 2* **1997**, 921.

(83) (a) Yoshifuji, M.; Sasaki, S.; Niitsu, T.; Inamoto, N. *Tetrahedron Lett.* **1989**, 30, 187. (b) Yoshifuji, M.; Sasaki, S.; Inamoto, N. *J. Chem. Soc., Chem. Commun.* **1989**, 1732. (c) Yoshifuji, M.; Niitsu, T.; Shiomi, D.; Inamoto, N. *Tetrahedron Lett.* **1989**, 30, 5433. (d) El Ouattib, R.; Ballivet-Tkatchenko, D.; Etemad-Moghadam, G.; Koenig, M. *J. Organomet. Chem.* **1993**, 453, 77. (e) Alberti, A.; Benaglia, M.; Della Bona, M. A.; Guerra, M.; Hudson, A.; Macciantelli, D. *Res. Chem. Intermed.* **1996**, 22, 381. (f) Toyota, K.; Nakamura, A.; Yoshifuji, M. *Chem. Commun.* **2002**, 3012.

Scheme 21. Reaction of 1,3-Phosphametalloallenes with H_2O and MeOH

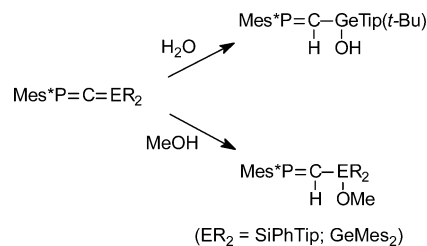


Chart 5. Stable Azasilaallenes

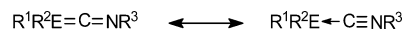


(Tbt = 2,4,6-[(Me_3Si)₂CH]₃C₆H₂)

(R = 2,4,6-*i*-Pr₃C₆H₂, Mes*, Tbt)

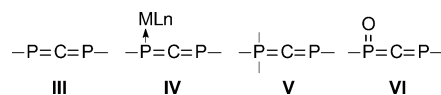
(R' = 2,6-*i*-Pr₂C₆H₃, Ad)

Chart 6. Structure of $\text{R}^1\text{R}^2\text{ECNR}^3$



(E = Si, Sn)

Chart 7. Neutral, Trivalent, Phosphorus-Containing Diphosphaallenes

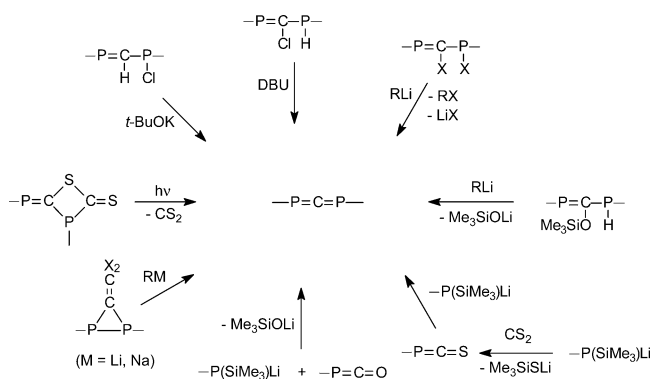
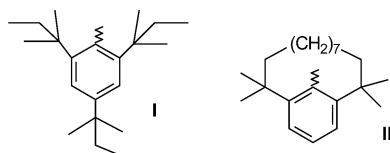
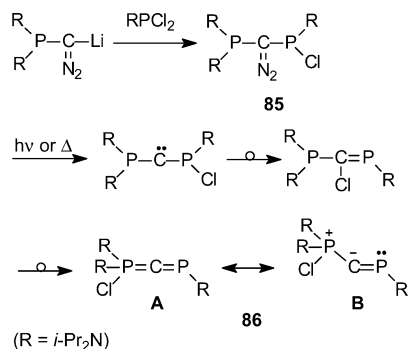


species bear bulky protecting groups such as 2,6-di-*tert*-butylphenyl, Mes*, 2,4,6-tri-*tert*-pentylphenyl (**I**), (Me_3Si)₃C, and 2,2,12,12-tetramethylbicyclo[11.3.1]heptadeca-1(17),13,15-trien-17-yl (**II**) (Chart 8).^{83f}

$1\sigma^2,3\sigma^2$ -Diphosphaallenes exhibit chemical shifts at low field for both phosphorus (ranging from 140 to 169 ppm) and sp carbon nuclei (around 275 ppm) with a large coupling constant $^1J_{\text{PC}}$ of about 58 Hz.^{10a}

The sole X-ray structure determination⁸⁴ of a $1\sigma^2,3\sigma^2$ -diphosphaallene reveals a PCP bond angle of 172(5)°, indicating a slight, but nevertheless significant, deviation from linearity of the PCP backbone in $\text{Mes}^*\text{P}=\text{C}=\text{PMes}^*$ (**82**). This angle contraction should reduce the interactions between the huge Mes* groups. Their mutual orientation (83.0°), which is almost orthogonal with respect to the PP axis, affords an important criterion for describing the $\text{P}=\text{C}=\text{P}$ bonding system as a

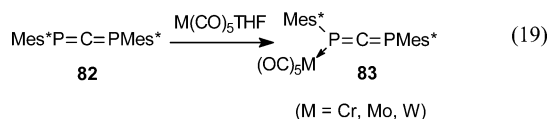
(84) Karsch, H. H.; Reisacher, H.-H.; Müller, G. *Angew. Chem., Int. Ed. Engl.* **1984**, 23, 618.

Scheme 22. Different Routes to $1\sigma^2,3\sigma^2$ -DiphosphaallenesChart 8. Stabilizing Bulky Groups for $1\sigma^2,3\sigma^2$ -DiphosphaallenesScheme 23. From (Phosphino)(chlorophosphino)diazomethane **85** to Diphosphaallene **86**

heteroallene, since allenes adopt comparable geometry. The shortening of the P=C bonds (1.635(8) and 1.630(8) Å) relative to isolated P=C(sp²) bonds (1.68–1.72 Å)^{6,85} presumably reflects the special electronic characteristics of the heteroallene and the smaller bond radius of the sp-hybridized carbon atom.

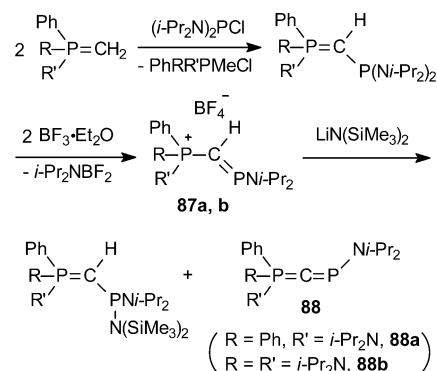
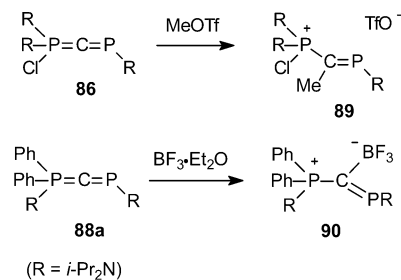
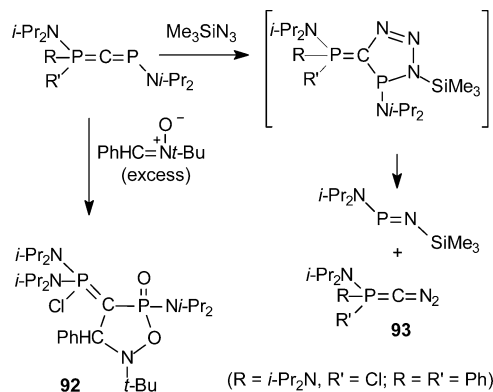
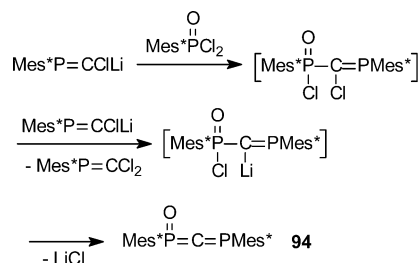
The reactivity of $1\sigma^2,3\sigma^2$ -diphosphaallenes has been discussed in a previous review.^{10a}

η^1 Transition-Metal Complexes of $1\sigma^2,3\sigma^2$ -Diphosphaallenes. The treatment of the $1\sigma^2,3\sigma^2$ -diphosphaallene **82** with group 6 transition metal carbonyl derivatives is of particular interest, since it leads to the new class of η^1 transition-metal



complexes of diphosphaallenes (**83**).⁷⁶ The coordination to the group 6 metal takes place at the phosphorus atom in an η^1 fashion, as deduced from a chemical shift correlation^{76a} and the

(85) (a) Becker, G.; Becker, W.; Mundt, A. *Phosphorus Sulfur Relat. Elem.* **1983**, *14*, 267. (b) Appel, R.; Knoll, F.; Ruppert, I. *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 731. (c) Markovski, L. N.; Romanenko, V. P.; Ruban, A. V. In *Chemistry of Acyclic Compounds of Two-Coordinated Phosphorus*; Naukova Dumka: Kiev, Ukraine, 1988.

Scheme 24. Alternative Synthesis of $1\sigma^4,3\sigma^2$ -Diphosphaallenes **V**Scheme 25. Ylidic Character of $1\sigma^4,3\sigma^2$ -Diphosphaallenes **86** and **88a**Scheme 26. Dipolarophile Behavior of $1\sigma^4,3\sigma^2$ -Diphosphaallenes **86** and **88a**Scheme 27. Synthesis of Mes*(O)P=C=PMes* (**94**)

phosphorus–tungsten coupling constant ($^1J_{PW} = 273$ Hz) in ³¹P NMR spectrum of the tungsten compound (eq 19).^{76a,b}

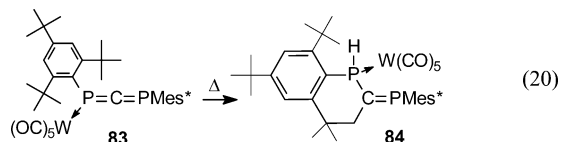
Complexes **83** exhibit two doublets at chemical shifts between 125 and 185 ppm in the ³¹P NMR spectrum for σ^3 -P and around 132 ppm for σ^2 -P with a mean coupling constant $^2J_{PP}$ of 37.4 Hz.

Compound **83** (M = W) underwent a hydrogen migration from the carbon to the phosphorus atom when heated in refluxing toluene to afford the carbon–carbon-coupled tetrahydro-1-phosphanaphthalene complex **84** (eq 20).^{76b}

Table 3. ^{31}P and ^{13}C NMR Spectroscopic Data (δ in ppm and J in hertz) and Selected Structural Parameters (Bond Lengths (Å) and Bond Angles (deg)) for Compounds **86**^{77a} and **88a** and **88b**^{77b}

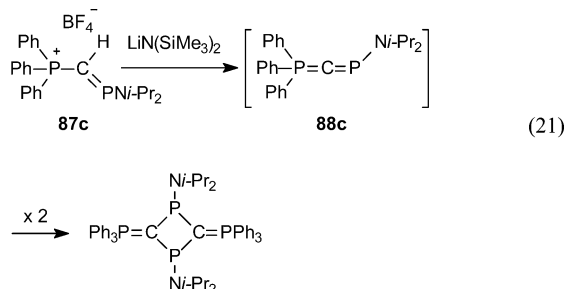
$\sigma^4, \sigma^2\text{-P=C=P}$	$\delta(^{31}\text{P}(\sigma^2/\sigma^4))$ ($^2J_{\text{PP}}$)	$\delta(^{13}\text{C})$ ($^1J_{\text{CP}}$)	$d(\sigma^4\text{P=C})$	$d(\sigma^2\text{P=C})$	PCP angle
86	302.8/61.2 (240.1)	169.9 (36.5/9.7)	1.6503(13)	1.6429(13)	120.88(9)
88a	313/41 (190)	166.5 (37/14)	1.3684	1.641	115.0
88b	295/59 (166)	162.4	1.669	1.629	125.3

1 $\sigma^4,3\sigma^2$ -Diphosphaallenes. The photolysis or thermolysis of the (phosphino)(chlorophosphino)diazomethane species **85** gave the first stable $1\sigma^4,3\sigma^2$ -diphosphaallene, **86**^{77a} (Scheme 23), by the well-established 1,2-migration reaction of singlet carbenes,⁸⁶ which operates for phosphinocarbenes⁸⁷ and the consecutive 1,2-halogen shift associated with α -halophosphines.⁸⁸



$1\sigma^4,3\sigma^2$ -Diphosphaallene **86** was obtained as a single isomer, in nearly quantitative yield. However, the scope of this synthetic strategy is very limited in terms of starting materials (diazo precursors and chlorine migrating group). Deprotonation of phosphoniophosphaalkenes **87** (accessible by Grützmacher's procedure⁸⁹) with the bulky, but not reducing, lithium hexamethyldisilazide (LiHMDS) offered an alternative way to $1\sigma^4,3\sigma^2$ -diphosphaallenes **88** (Scheme 24).^{77b}

Although concurrent attack of LiHMDS at the σ^2 -phosphorus atom of the more acidic phosphoniophosphaalkene **87c** did not occur, the expected diphosphaallene **88c** could not be detected, since it readily underwent head-to-tail dimerization (eq 21).^{77b}



The $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of **86** and **88a,b** display two doublets in the regions expected for σ^2 - and σ^4 -phosphorus atoms.^{10a,90} The signals for the dicoordinate carbon atom appear as doublets of doublets at δ around 165 ppm (Table 3), chemical shifts approximately halfway between the values reported for carbodiphosphoranes (σ^4, σ^4 -diphosphaallenes) ($\delta(^{13}\text{C})$ 0–20 ppm)⁹¹ and σ^2, σ^2 -diphosphaallenes **III**.^{10a} The PCP bond angle

(86) (a) Bourissou, D.; Bertrand, G. *Chem. Rev.* **2000**, *100*, 39. (b) Ford, F.; Yuzawa, T.; Platz, M. S.; Matzinger, S.; Füllscher, M. *J. Am. Chem. Soc.* **1998**, *120*, 4430. (c) Sulzbach, M.; Platz, M. S.; Schaefer, H. F., III; Hadad, C. M. *J. Am. Chem. Soc.* **1997**, *119*, 5682. (d) Keating, A. E.; Garcia-Garibay, M. A.; Houk, K. N. *J. Am. Chem. Soc.* **1997**, *119*, 10805. (e) Sander, W.; Bucher, G.; Wierlacher, S. *Chem. Rev.* **1993**, *93*, 1583.

(87) Baceiredo, A.; Igau, A.; Bertrand, G.; Menu, M. J.; Dartiguenave, Y.; Bonnet, J. J. *J. Am. Chem. Soc.* **1986**, *108*, 7868.

(88) (a) Kolodiaznyy, O. I. *Russ. Chem. Rev.* **1997**, *66*, 225. (b) Appel, R.; Huppertz, M.; Westerhaus, A. *Chem. Ber.* **1983**, *116*, 114.

(89) Grützmacher, H.; Pritzkow, H. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 740.

(90) *CRC Handbook of Phosphorus-31 Nuclear Magnetic Resonance Data*; Tebby, J. C., Ed.; CRC: Boca Raton, FL, 1991.

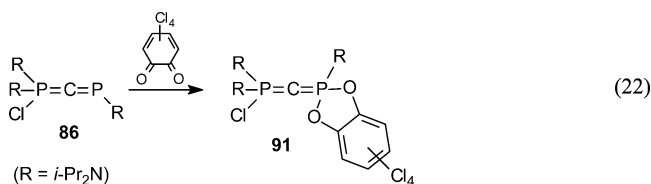
(91) Johnson, A. W.; Kaska, W. C. O.; Starzewski, K. A.; Dixon, D. A. In *Ylides and Imines of Phosphorus*; Johnson, A. W., Ed.; Wiley-Interscience: New York, 1993; pp 64–68.

(120.88°) and the planar arrangement of the NPCP fragment in **86** point to sp^2 hybridization of the carbon atom (form **B** in Scheme 23).

The X-ray molecular structure of **86** showed an *E* configuration of the σ^2 -P=C bond and a markedly shorter P=C distance (1.64 Å) with respect to an isolated P=C bond length,^{6,85} but this value was comparable with that observed for $\text{Mes}^*\text{P}=\text{C}=\text{PMes}^*$.⁸⁴ Interaction of a lone pair of electrons at the carbon atom with the σ^4 -P atom is confirmed by the short P–C bond length (1.65 Å) and the eclipsed position of the σ^4 -P–Cl bond and the CPN fragment. This so-called negative hyperconjugation⁹² transfers the electron density from the occupied sp^2 orbital on the carbon atom to the energetically low-lying σ^* orbital of the σ^4 -P–Cl bond.⁹³ Close geometric parameters were determined for compounds **88a,b** (Table 3). Therefore, derivatives **86** and **88a,b** can be considered as heteroallenes.

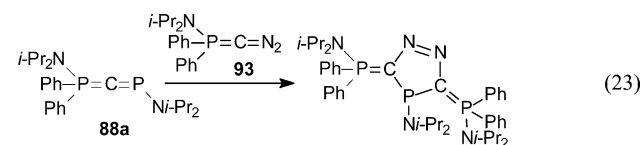
Owing to the presence of a ylidic carbon atom, **86** reacted with an alkylating agent such as methyl trifluoromethanesulfonate to give the expected *C*-phosphoniophosphaalkene **89**^{77a} as only one isomer (59% yield), whereas **88a** combined with the Lewis acid BF_3 to form the corresponding complex **90**^{77b} (Scheme 25).

A formal [1 + 4] cycloaddition between the lone pair of electrons at the σ^2 -phosphorus of diphosphaallene **86** and tetrachloro-*o*-benzoquinone afforded carbodiphosphorane **91** (eq 22).



Compounds **86** and **88a** reacted as dipolarophiles in the [2 + 3] cycloaddition reactions with a nitrene^{77a} and trimethylsilyl azide, eventually leading to phosphonic amide **92** with excess nitrene and a mixture of the iminophosphane *i*-Pr₂NP=NSiMe₃ and diazomethylenephosphorane **93**, respectively (Scheme 26).⁷⁷

Further [2 + 3] cycloaddition between **88a** and diazomethylenephosphorane **93** was observed (eq 23).^{77b}

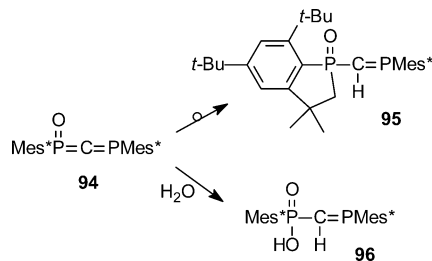
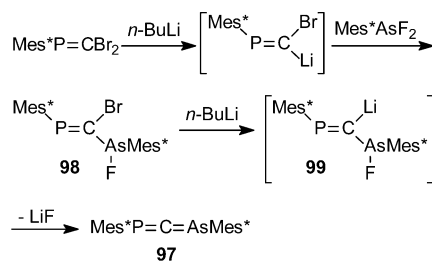
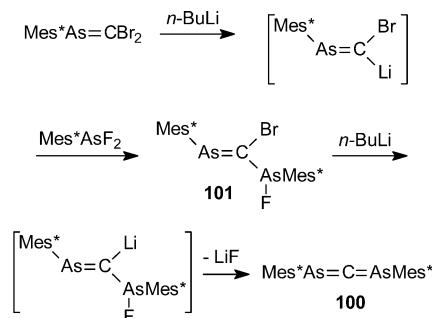


1 $\sigma^3,3\sigma^2$ -Diphosphaallenes. We recently have been successful in the synthesis of a new $1\sigma^3,3\sigma^2$ -diphosphaallene, $\text{Mes}^*(\text{O})\text{P}=\text{C}=\text{PMes}^*$ (**94**).⁷⁸ A methylene(oxo)phosphorane unit, of which only two representatives have been described to date,⁹⁴ is

(92) Schleyer, P. v. R.; Kos, A. J. *Tetrahedron* **1983**, *39*, 1141.

(93) Grützmacher, H.; Pritzkow, H. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 99.

(94) (a) Appel, R.; Casser, C. *Tetrahedron Lett.* **1984**, *25*, 4109. (b) Appel, R.; Knoch, H.; Kunze, H. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 157.

Scheme 28. Reactivity of 1 σ^3 ,3 σ^2 -Diphosphaallene **94**Scheme 29. Synthesis of Phospharsaallene Mes*P=C=AsMes* (**97**)Scheme 30. Synthesis of 1,3-Diarsaallene **100**

embodied in the heteroallene structure. Treatment of the phosphonic dichloride Mes*(O)PCl₂ with the (phosphaalkenyl)-lithium species Mes*P=CClLi afforded **94** in 40% yield. The reaction probably involves the initial formation of a phosphaalkenylphosphane oxide. A rapid CCl/CLi exchange then leads to Mes*P=CCl₂ and the related (chlorodiphosphaapropenyl)lithium compound. The latter affords the target compound by loss of LiCl (Scheme 27).

The ³¹P NMR spectrum of **94** displays an AX system at δ 261.4 (σ^2 -P) and 117.3 ppm (σ^3 -P) with a coupling constant $^2J_{PP}$ of 30.5 Hz. A large high-frequency shift of \sim 125 ppm was observed for the σ^2 -P in comparison with the values reported for the related 1 σ^2 ,3 σ^2 -diphosphaallene Mes*P=C=PMes* (**82**)⁷⁵ and diphosphaallene complexes **83**.^{76a} The signal of the σ^3 -phosphorus atom is slightly shifted to lower frequency with respect to the values observed for diphosphaallene complexes **83** (δ (³¹P) 125–185 ppm)^{76a} and for Mes*(O)P=C(SiMe₃)R (δ (³¹P) 153.7 ppm (R = Ph),^{94a} 161.1 ppm (R = Me₃Si)^{94b}). The sp-hybridized carbon atom gives rise to a doublet of doublets at 229.1 ppm ($^1J_{CP(O)} = 177.4$, $^1J_{CP} = 46.8$ Hz). The rotation barrier for the Mes* bonded to the σ^2 -phosphorus atom was evaluated to be 12.2 kcal mol⁻¹ by dynamic ¹H NMR spectroscopy.

Although it is stable for months in the solid state, methylene-(oxo)phosphorane **94** slowly rearranged within 1 day at room temperature in solution into the (phosphaalkenyl)phosphine oxide **95**. Water added selectively to the more reactive σ^3 -P=C double bond to give the (phosphaalkenyl)phosphinic acid **96** (Scheme 28).

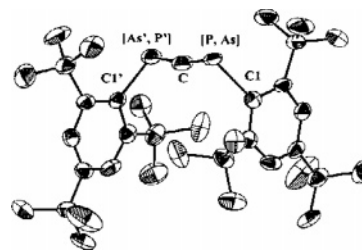


Figure 6. Molecular view of Mes*P=C=AsMes* in the solid state.

1,3-Phospharsaallenes

In marked contrast, the field of allene analogues of arsenic has been less investigated. As mentioned previously, only the transient arsaallene HAS=C=CH₂^{56b} and arsabutatriene TsiAs=C=C=CPh₂ (Tsi = (Me₃Si)₃C)^{56c} have been postulated as intermediates. The first stable heteroallene of arsenic, which is the phospharsaallene Mes*P=C=AsMes* (**97**),⁹⁵ incorporates a σ^2 -phosphorus atom. Coupling Mes*P=CBrLi with Mes*AsF₂ afforded the 2,3-bromofluorophospharsapropene **98**, probably as the Z isomer. Conversion of phospharsapropene **98** to phospharsaallene **97** was achieved by its treatment with *n*-butyllithium at -90 °C. The organolithium intermediate **99** thus formed lost LiF to give in nearly quantitative yield the expected phospharsaallene **97** (Scheme 29).

Although the phosphorus and arsenic atom positions could not be defined precisely in the X-ray molecular structure,⁹⁵ a near-linear triatomic arrangement with the central allenic carbon bonded to two Mes*P or Mes*As groups was obvious (Figure 6). The recent fully optimized geometry of HP=C=AsH, determined with the B3LYP hybrid functional and the 6-311G-(d,p) basis set,⁹⁶ showed the P=C and As=C bond lengths to be respectively 1.644 and 1.769 Å, the carbon bond angle to be 170.20°, and the HASPH dihedral angle to be 90.37°.

The allene-like structure of **97** was unambiguously established by its ¹³C and ³¹P NMR spectra. The sp carbon and the double-bonded phosphorus nuclei resonated at characteristic low field with chemical shifts of 299.5 (d, $^1J_{CP} = 75.1$ Hz) and 159.7 ppm, respectively. A rotational barrier of 13.67 kcal mol⁻¹ for the Mes* groups, comparable to those reported for Mes*P=C=PMes*^{83a} and for Mes*(O)P=C=PMes*,⁷⁸ was determined by dynamic ¹H NMR spectroscopy. The different ionizations on the PE spectrum of phospharsaallene **97** were fully assigned by confronting experimental and theoretical results (vide infra).⁹⁶

1,3-Diarsaallenes

The synthetic method for the first stable 1,3-diarsaallene Mes*As=C=AsMes* (**100**) parallels the previously described procedures for phosphametalloallenes **68**, **73**, and **76** and the phospharsaallene **97**.⁹⁷ Successive treatment of Mes*As=CBrLi with *n*-BuLi and Mes*AsF₂ at -80 °C afforded the bromodiarsapropene **101**, which in turn gave diarsaallene **100** in good yield upon addition of *n*-BuLi at low temperature (Scheme 30).

Although a disorder of the whole molecule was observed in the X-ray structure determination (Figure 7),⁹⁷ the study revealed a deviation from linearity of the AsCAs skeleton (175.6(6) and

(95) Ranaivonjatovo, H.; Ramdane, H.; Gornitzka, H.; Escudicé, J.; Satgé, J. *Organometallics* **1998**, *17*, 1631.

(96) Miqueu, K.; Sotiropoulos, J.-M.; Baylère, P.; Joantéguy, S.; Pfister-Guillouzo, G.; Ranaivonjatovo, H.; Escudicé, J.; Bouslikhane, M. *J. Mol. Struct.* **2004**, *690*, 53.

(97) Bouslikhane, M.; Gornitzka, H.; Escudicé, J.; Ranaivonjatovo, H.; Ramdane, H. *J. Am. Chem. Soc.* **2000**, *122*, 12880.

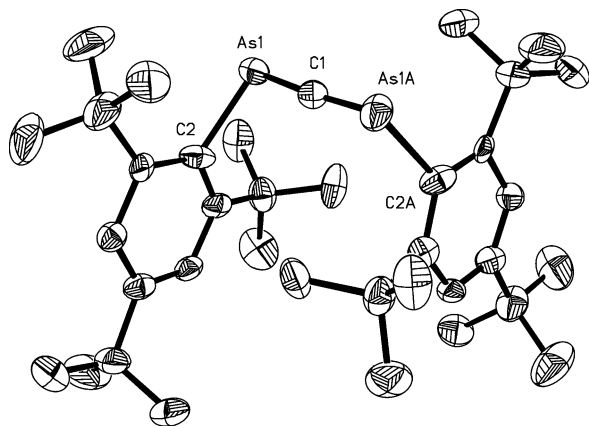


Figure 7. X-ray structure of $\text{Mes}^*\text{As}=\text{C}=\text{AsMes}^*$ drawn at the 50% probability level.

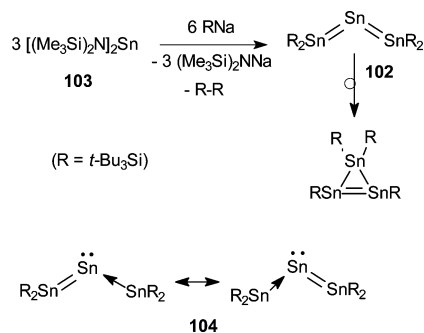
$176.2(13)^\circ$), which is less pronounced than in the PCP unit in $\text{Mes}^*\text{P}=\text{C}=\text{PMes}^*$ ($172.6(5)^\circ$). The torsion angle $(\text{Mes}^*)\text{-CAsAsC}(\text{Mes}^*)$ amounted to $77.6(6)$ and $78.3(9)^\circ$.⁹⁷ The $\text{As}=\text{C}$ bonds ($1.7584(9)$ and $1.7575(17)$ Å) were markedly shorter compared to those found in acyclic arsaalkenes ($1.794\text{--}1.876$ Å),^{7,60} due to the smaller bond radius of the sp -hybridized carbon atom and the special electronic characteristics of the heteroallene. These findings substantiate the description of the bonding system as a heteroallene. The computed geometry of the parent diarsaallene $\text{HAs}=\text{C}=\text{AsH}$ ($d(\text{As}=\text{C}) = 1.766$ Å, $\text{As}-\text{C}-\text{As} = 169.7^\circ$, $\text{H}-\text{As}-\text{As}-\text{H} = 90.42^\circ$) is in agreement with that found for arsaallene **100**. The huge Mes^* groups and the packing effects in the solid state could explain the small discrepancy observed between experimental and calculated geometric parameters.

The characteristic ^{13}C NMR signal at very low field (δ 297.5 ppm) also supports the assigned structure.⁹⁷ The stabilization of such derivatives stems from the steric congestion of the substituents, as evidenced by the large rotational barrier (12.9 kcal mol^{-1}) at the Mes^* groups determined by dynamic ^1H NMR studies.⁹⁷

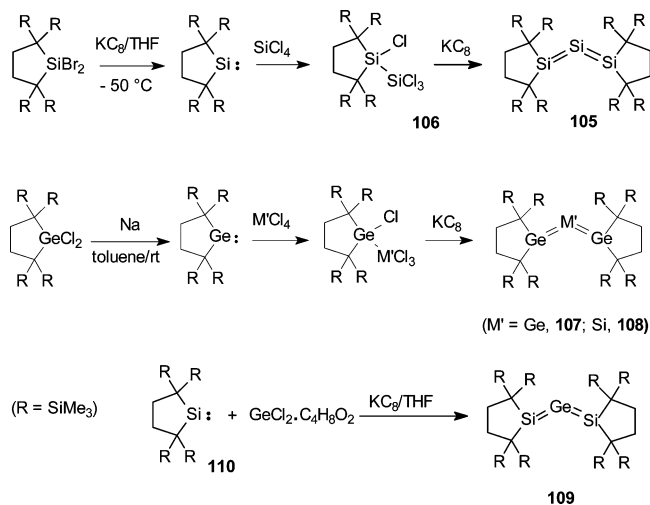
Computational studies (B3LYP hybrid functional and the 6-311G(d,p) basis set) have been performed on the model compounds $\text{HP}=\text{C}=\text{PH}$, $\text{HP}=\text{C}=\text{AsH}$, and $\text{HAs}=\text{C}=\text{AsH}$ in order to determine the different interactions which take place in such heteroallenes, particularly between the π -bond and the pnictogen lone pair n_{Pn} ($\text{Pn} = \text{P}, \text{As}$). HOMO–LUMO gaps of 4.97, 4.49, and 4.57 eV, respectively, were found.⁹⁶ The smallest values obtained for phospharsa- and diarsaallenes imply a greater reactivity compared to that of the diphosphaallenes, particularly in $[2 + 2]$ cycloadditions. The calculations extended to phospho- and arsalkenes $-\text{Pn}=\text{C}<$ give HOMO–LUMO gaps of 5.06 and 5.64 eV, respectively. A higher reactivity can thus be expected for the $\text{Pn}=\text{C}$ double bond of heteroallenes $-\text{Pn}=\text{C}=\text{Pn}-$ compared to that of phospho- or arsaalkenes.

The UV photoelectron spectra of **97** and **100** recorded at 135 and 178 °C, respectively, are very similar.⁹⁶ Comparison of the experimental and theoretical results obtained from calculations on the model compounds ($\text{RP}=\text{C}=\text{AsR}$ and $\text{RAs}=\text{C}=\text{AsR}$, $\text{R} = 2,6\text{-dimethylphenyl}$) allowed an assignment of the different ionizations in the PE spectra.⁹⁶ This assignment needs to envisage rotamers, in agreement with the dynamic ^1H NMR study, which showed that the aryl groups were not frozen and underwent a slow rotation in a gear mode. This rotation is restrained because of the steric hindrance and has a barrier much higher than the energy difference between the rotamers having dihedral angles at 45 and 90° . The bands at 7.9 eV (**97**)/ 7.8 eV

Scheme 31. Tristannaallene **102**



Scheme 32. Silicon and Germanium Trimetallaallenes



(**100**) correspond to the removal of an electron from the $\pi_{\text{Pn}=\text{C}} + n_{\text{Pn}}$ orbital and those at 9.0 eV (**97**/**100**) and 9.8 eV (**97**)/9.5 eV (**100**) are mainly assigned to the removal of an electron from the $\pi_{\text{Pn}=\text{C}} + n_{\text{Pn}}$ orbital mixed with the $\sigma_{\text{Pn}=\text{C}}(\text{allenic})$ orbital of rotamers at 45 and 90° , respectively. The bands at 8.3 and 8.5 eV are associated with the supermesityl groups. From these very close PES spectra, a similar reactivity can be expected for heteroallenes **97** and **100**.

Heteroallenes $\text{E}_{14}=\text{E}'_{14}=\text{E}''_{14}$

To finish this review about heteroallenes, we will report the results of Wiberg and Kira in the field of trimetallaallenes $\text{E}_{14}=\text{E}_{14}$. Thus, tristannaallene **102**,⁹⁸ obtained from stannylene **103** and RNa ($\text{R} = t\text{-Bu}_3\text{Si}$), has been isolated. It rearranges at ambient temperature to the corresponding cyclotristannene and, according to its ^{119}Sn NMR spectrum and X-ray structural analysis, its bonding situation in **102** is best described by the resonance formulas **104** (Scheme 31).

The first trisilaallene, **105**, a derivative with a formal sp Si atom, was synthesized by reduction of the tetrachlorodisilane **106** with potassium graphite and isolated as a thermally very stable but air-sensitive compound (Scheme 32).^{99a} The trigermanium analogue **107** and the 1,3-digermasilaallene **108** have been obtained by a similar route,^{99b} whereas the 1,3-disilager-

(98) Wiberg, N.; Lerner, H.-W.; Vasisht, S.-K.; Wagner, S.; Karaghiosoff, K.; Nöth, H.; Ponikvar, W. *Eur. J. Inorg. Chem.* **1999**, 1211.

(99) (a) Ishida, S.; Iwamoto, T.; Kabuto, C.; Kira, M. *Nature* **2003**, *421*, 725. (b) Iwamoto, T.; Masuda, H.; Kabuto, C.; Kira, M. *Organometallics* **2005**, *24*, 197. (c) Iwamoto, T.; Abe, T.; Kabuto, C.; Kira, M. *Chem. Commun.* **2005**, 5190. (d) Kira, M.; Ishida, S.; Iwamoto, T.; Kabuto, C. *J. Am. Chem. Soc.* **1999**, *121*, 9722.

maallene derivative **109**^{99c} was prepared by reduction of a mixture of silylene **110**^{99d} and $\text{GeCl}_2 \cdot (\text{dioxane})$.

X-ray analyses of these heteroallenes showed bent-allenic structures with a $E_{14}=E_{14}=E_{14}$ bond angle of $122.6\text{--}136.5^\circ$. A fluxional process was observed in solution. A significant conjugation between the $E=E'$ double bonds occurs. The ^{29}Si NMR resonances for the central silicon atom were observed, as expected, at very low field (236 ppm in $\text{Ge}=\text{Si}=\text{Ge}$ and 157 ppm in $\text{Si}=\text{Si}=\text{Si}$).

Conclusion

The results in the field of 1-heteroallenes with one group 14 and 15 element deserve some comment. In the case of group 14 elements with the same type of groups on carbon and on group 14 element (generally a bulky substituted aromatic group), sila- and germaallenes $>E=C=C<$ ($E = \text{Si}, \text{Ge}$) show similar behavior and both are rather stable.^{16,17} However, a great difference is observed with the stannaallene analogue **15**,²² which cannot be stabilized even at low temperature.

The same trend is observed in group 15 with exactly the same groups on the P, As, Sb, and C atoms; both phosphaaallene **26**⁴⁴ and arsaallene **60**⁶⁰ are thermally stable, whereas the stibaallene analogue **65**⁶¹ cannot be observed. Thus, stannaallene and stibaallene were characterized only by their chemical behavior. These results confirm the well-known gap between the third and fourth rows of the periodic table. Moreover, a great difference is observed between 1-heteroallenes with a heavier group 14 and 15 element of the fourth row, since a very easy dissociation of the $\text{Sn}=\text{C}$ bond is observed, whereas the $\text{Sb}=\text{C}$ bond dimerizes. Thus, still bulkier groups or groups with other electronic effects are necessary to stabilize such heavy heteroallenes.

Within the same row, $-E_{15}=\text{C}=\text{C}<$ derivatives are much more stable and less reactive than the corresponding $>E_{14}=\text{C}=\text{C}<$ compounds. Moreover, X-ray structure determinations show that the geometry of heteroallenes $-E_{15}=\text{C}=\text{C}<$ fits rather well with that expected for an allene-like structure. The comparison of X-ray data shows that 1-phosphaallenes or

1-arsaallenes are closer to an allenic structure than 1-silaallenes or 1-germaallenes, although large shortenings (about 10–12%) of the $\text{Si}=\text{C}$ or $\text{Ge}=\text{C}$ double bonds in relation to the standard corresponding single bonds are noticed.

Heteroallenes with one doubly bonded element of group 15, particularly phosphorus, are by far more abundant than their analogues with a heavier group 14 element. This is mainly due to $E_{15}=\text{C}$ being less reactive than the $E_{14}=\text{C}$ double bond, which makes them easier to stabilize and allows various types of synthetic routes: initial creation of both $E_{15}=\text{C}$ and $\text{C}=\text{X}$ double bonds can be planned, whereas in the case of $E_{14}=\text{C}=\text{X}$ derivatives, the $E_{14}=\text{C}$ double bond must be formed in the final step.

As expected, very few stable heteroallenes of the type $E_{14(15)}=\text{C}=\text{E}_{16}$ have been isolated or even characterized. Their stabilization is much more difficult, due to the absence of a substituent on the E_{16} element.

Efforts should now be directed to the synthesis of new heteroallenes containing the heaviest elements of not only groups 14 (Sn, Pb) and 15 (Sb, Bi) but also elements of group 13 such as boron. The study of the reactivity of all these heteroallenes needs further development. The results should be very interesting, due to the various possibilities of reactions on the two cumulative double bonds, and may even lead to applications. In this connection we note the diphosphinidenecyclobutenes⁴⁷ derived from 1-phosphaallenes can serve as ligands in transition-metal complexes that have very good catalytic properties.

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