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$Mes_2Ge{=}C{=}PAr$: The First Germaphosphaallene

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The first germaphosphaallene, **3**, has been obtained by debromofluorination of the (fluorogermyl)bromophosphaalkene **7** and characterized by ^{31}P NMR (240 ppm) and ^{13}C NMR (280.9 ppm for the allenic carbon) at low temperature. Methanol and methyllithium react exclusively with the Ge═C double bond to afford the corresponding adducts **9** and **10**. In the absence of a trapping reagent, **3** gives two types of dimer, **13a** (involving two Ge═C bonds) and **14a** (involving one Ge═C and one P═C bond).

Introduction

Many stable doubly-bonded compounds of the group 14 and 15 elements such as "heteroalkenes" >M═C< (M: Si,[1] Ge,[2] Sn[3]) or −P═C<[4] have been synthesized and studied, but very little is known about heavy analogs of cumulenes in which one or two atoms of the first row have been replaced by elements such as Si, Ge, and Sn and P, As, and Sb, respectively. Thus, only two "heavy allenes" of the type >M═C═X with a group 14 element, the silaallene **1** obtained by West[5] and the stannaketenimine **2** prepared by Grützmacher,[6] have been structurally characterized to date (Chart 1).

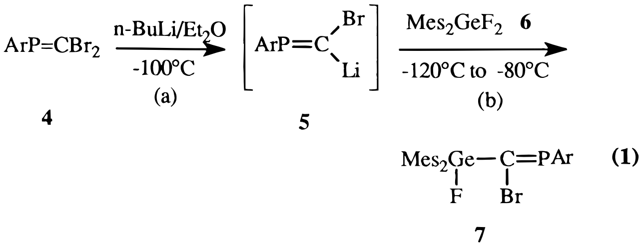
With a group 15 element, only some phosphaallenes of the type −P═C═X[4d,7] (X: C, O, N, P, S) have been prepared.

We report here the synthesis and some aspects of the reactivity of the first metastable allene that contains two heavy elements of group 14 and 15, *Ge,Ge*-dimesityl-*P*-(2,4,6-tri-*tert*-butylphenyl)germaphosphaallene **(3)** (Chart 2).

Results and Discussion

We have chosen the mesityl and "supermesityl" groups as substituents since they are widely used to provide steric stabilization of low-coordinate derivatives of germanium[2] and phosphorus.[4] As the simultaneous creation of >Ge═C< and −P═C< double bonds seems unlikely, we thought that the best strategy to synthesize **3** was first form the −P═C< double bond since it is generally much less reactive than the >Ge═C< double bond and thus, hopefully, would be inert during the rest of the synthesis.

a. Synthesis and Characterization of 3. We have prepared the precursor **7** according to the process used by Bickelhaupt for the synthesis of $ArP{=}C(Br)MMe_3$ (M: Si, Ge, Sn):[8] addition of *n*-butyllithium at low temperature to the dibromophosphaalkene **4**[8a] and then quenching the resulting lithio compound **5** with dimesityldifluorogermane **(6)** (eq 1).



$$ArP{=}CBr_2 \xrightarrow[-100\,°C\ (a)]{n\text{-}BuLi/Et_2O} [ArP{=}C(Br)Li] \xrightarrow[-120\,°C\ to\ -80\,°C\ (b)]{Mes_2GeF_2\ \mathbf{6}} Mes_2Ge(F){-}C(Br){=}PAr \quad (1)$$

As reaction b of eq 1 is slow, the best yield in **7** was obtained when the reaction mixture was stirred for 1 h at −80 °C, after addition of the difluorogermane **6** to **5**

[⊗] Abstract published in *Advance ACS Abstracts,* June 1, 1996.

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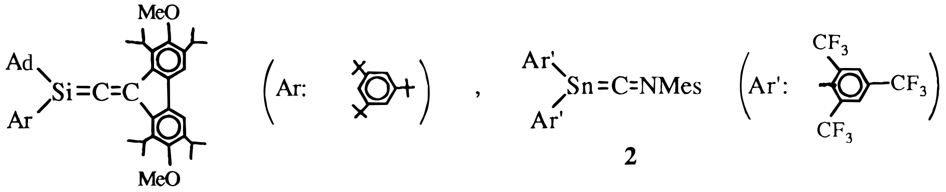
Chart 1[a]



1

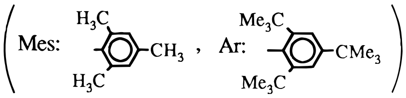
2

[a] Ad = adamantyl.

Chart 2

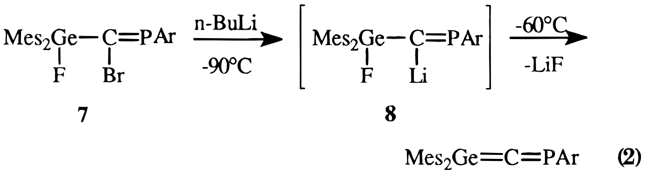
$Mes_2Ge{=}C{=}PAr$

3



at −120 °C. At this temperature the carbenoid **5** is stable. **7** can also be obtained in one pot by adding two equiv of *n*-butyllithium to a mixture of **4** and **6** in Et_2O since at −120 °C *n*-butyllithium does not react with the germanium−fluorine bond of **6**.

The debromofluorination of **7** to give germaphosphaallene **3** was effected with *n*-butyllithium at low temperature (a similar method to create a >Ge=C< double bond was used by Wiberg for the formation of transient germenes[9]). The reaction, followed by ^{31}P NMR between −85 °C and room temperature, showed the immediate formation of the lithio compound **8**, as shown by a doublet at 397.4 ppm ($^3J_{PF}$ = 16.9 Hz). Elimination of LiF occurred at −60 °C to give the expected germaphosphaallene **3** (eq 2).



$$Mes_2Ge(F){-}C(Br){=}PAr \xrightarrow[-90°C]{n\text{-BuLi}} [Mes_2Ge(F){-}C(Li){=}PAr] \xrightarrow[-LiF]{-60°C} Mes_2Ge{=}C{=}PAr \quad (2)$$

7 **8** **3**

According to the ^{31}P NMR spectrum, **3** was formed in about 65−70% yield and was stable below −50 °C. Its structure was proved by low field shifts in ^{31}P NMR (δ 240.0 ppm, characteristic of a P(II) derivative) and in ^{13}C NMR (δ 280.9 ppm, d, $^1J_{CP}$ = 54.3 Hz for the allenic carbon). Similar chemical shifts were observed for the allenic carbon of diphosphaallene ArP=C=PAr (276.2 ppm, $^1J_{CP}$ = 58 Hz[10]) and arsaphosphaallene ArP=C=AsAr (299.5 ppm, $^1J_{CP}$ = 75.1 Hz[11]). The structure of **3** was also proved by its chemical reactivity. Addition of methanol or methyllithium followed by methanolysis at −40 °C afforded the new phosphaalkenes **9** and **10**, respectively. A regiospecific reaction was observed with exclusive addition to the Ge=C double bond according to the $Ge^{\delta+}{=}C^{\delta-}$ polarity (Scheme 1).

9 and **10** have been identified by their physicochemical data as well as by their independent synthesis from phosphaalkene **12**:[8a] successive addition of *n*-butyllithium and of **6** at low temperature afforded **11**; further reaction with MeOLi or methyllithium gave **9** and **10**, respectively, in nearly quantitative yield (Scheme 1); addition of MeLi or MeOLi on the P=C bond is not observed. The formation of **3** by reacting **11** with MeLi or LDA does not occur.

b. Dimerization of 3. In the absence of trapping reagent, the germaphosphaallene **3** gives two types of dimers: the "classical" head-to-tail dimer **13a** (dimerization between two Ge=C double bonds) and the unexpected dimer **14a** due to the cycloaddition between a Ge=C and a P=C double bond. **14a** is the major compound : 12/88 **13a**/**14a**.

13a and **14a** have completely different solubilities; **14a** is very soluble in Et_2O and other organic solvents (pentane, THF), whereas **13a** is poorly soluble and consequently was easily separated from the reaction mixture in the form of a yellow powder.

14a was characterized in ^{31}P NMR spectroscopy, showing an AX spectrum with the expected low field shift for the dicoordinate phosphorus atom (+269.5 ppm) and a signal at +61.3 ppm for the tricoordinate phosphorus atom with a large $^2J_{PCP}$ coupling constant (225.4 Hz) (Scheme 2).

From the large phosphorus−phosphorus coupling constant (225.4 Hz), it seems that the unsymmetrical isomer obtained is **14a** since the literature data show that $^2J_{PP}$ is generally around 15−30 Hz in cis structures such as **14b**, whereas it is larger than 100 Hz in trans structures such as **14a**[12] (Chart 3).

14a could not be obtained as a crystalline compound but only as a reddish, viscous oil which was air sensitive due to the presence of the Ge=C double bond. Addition of methyllithium to the Ge=C unsaturation followed by methanolysis afforded derivative **15**, which was characterized. The AX system observed in the ^{31}P NMR spectrum with a signal at low field (352.6 ppm, $^2J_{PCP}$ = 112.9 Hz), characteristic of a dicoordinate phosphorus, proved that methyllithium reacted only with the Ge=C double bond. In ^1H NMR spectrum the *tert*-butyl and mesityl groups appeared as very broad signals. The extremely large steric congestion hinders the free rotation of these groups at room temperature. Broad signals were also observed for the *tert*-butyl groups in ^{13}C NMR spectrum.

The "classical" head-to-tail dimer **13** isolated immediately after dimerization was the trans isomer **13a** as proved by the ^1H NMR spectrum which displays two equivalent Ar and four equivalent mesityl groups. After 7 days at room temperature in solution, a mixture of **13a**/**13b** was observed in 42/58 ratio. The same ratio was obtained from **13a** after only 2 h of irradiation (254 nm). The thermodynamic equilibrium between **13a** and

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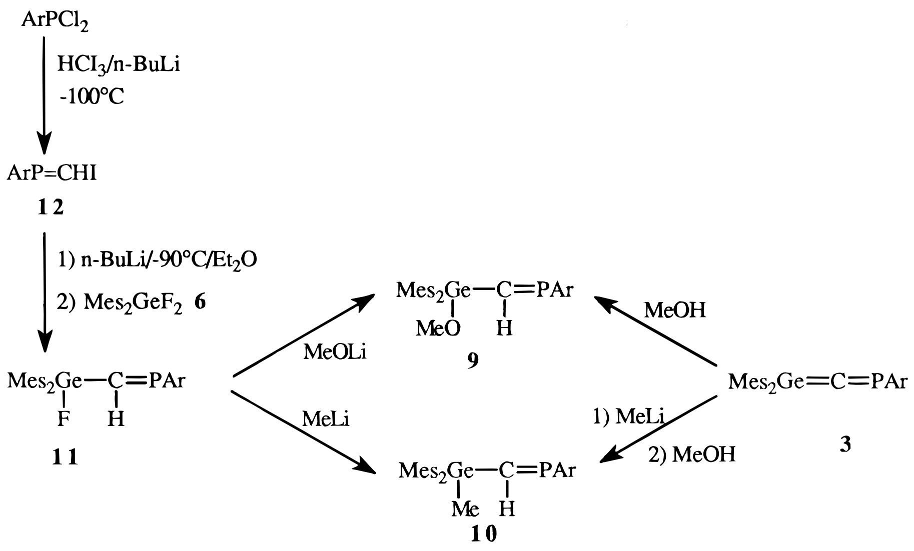
Scheme 1



Scheme 2

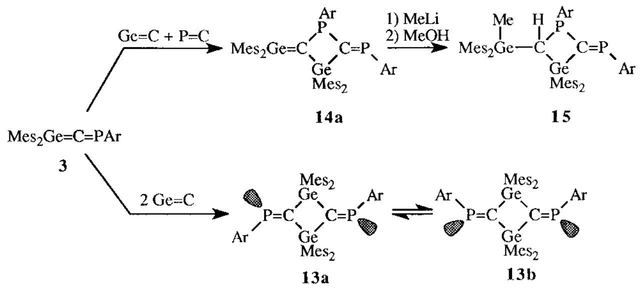
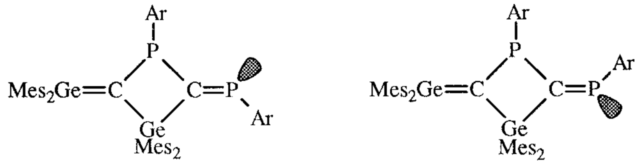
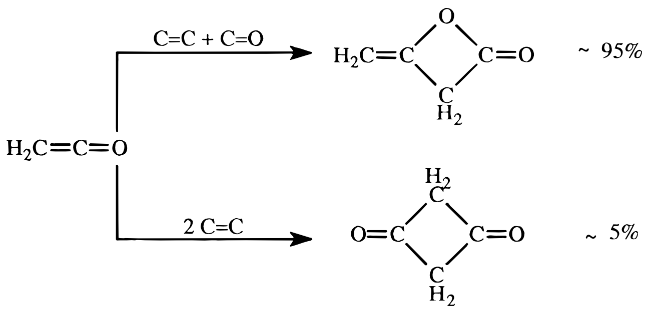


Chart 3



14a (trans) **14b** (cis)

Scheme 3



13b was unambiguously proved by a 2 h irradiation of pure **13b** leading again to the mixture **13a**/**13b** in 42/58 ratio.

The cis structure of **13b** was obvious from the ^{1}H NMR spectrum which exhibits very different mesityl groups: the ortho methyl groups on the mesityl cis to the aromatic rings are about 1 ppm high field shifted in relation to those on the mesityl trans to the aromatic rings (1.55 and 2.51 ppm); a large splitting was also observed for the aromatic protons of the mesityls (6.35 and 6.75 ppm). This large difference of chemical shift is of course due to their location cis or trans to the lone pairs or to the aromatic rings. Another argument for this attribution was given by the low-temperature ^{1}H NMR spectrum of **13b**: in the mesityl groups, the signals at high field for the *o*-Me (1.55 ppm) and the aromatic hydrogens (6.35 ppm) widen when the temperature decreases; at −45 °C, the signal of the *o*-Me even disappears completely. The widening of these signals is of course due to the slow rotation of the mesityl groups caused by the steric hindrance; thus, these signals can be attributed to the Mes groups cis to the Ar groups. On the contrary, the signals at 2.51 and 6.75 ppm corresponding respectively to the *o*-Me and aromatic H of the Mes groups cis to the lone pairs are not really affected at low temperature.

The isomerization of **13a** to **13b**, which is the major isomer when the thermodynamic equilibrium is established, seems surprising since the trans isomer **13a** should be a priori less hindered and, for this reason, more abondant. However, we may suppose that a folding of the four-membered ring along the Ge−Ge axis combined with a torsion around the P=C double bond could relieve the steric strain in **13b**.

In contrast to the unsymmetrical isomer **14a**, **13a**,**b** with only P=C double bonds are unreactive toward air and moisture and even toward methyllithium.

The two types of dimerization of **3**, although unexpected, have some precedent in the very similar behavior observed for ketene[13] with formation of both symmetrical and unsymmetrical dimers due to the cycloaddition between two C=C bonds or between one C=C and one C=O bond (Scheme 3).

However, the energy differences between lactone and dione formation transition structures are small and for example, with alkyl or aryl substituents on carbon instead of hydrogen, the dione product is generally the most important.[14] In phosphacumulenes, −P=C=X (X: O[15] or S[16]), different dimers are obtained depending on X. Thus phosphaketene undergoes a dimerization

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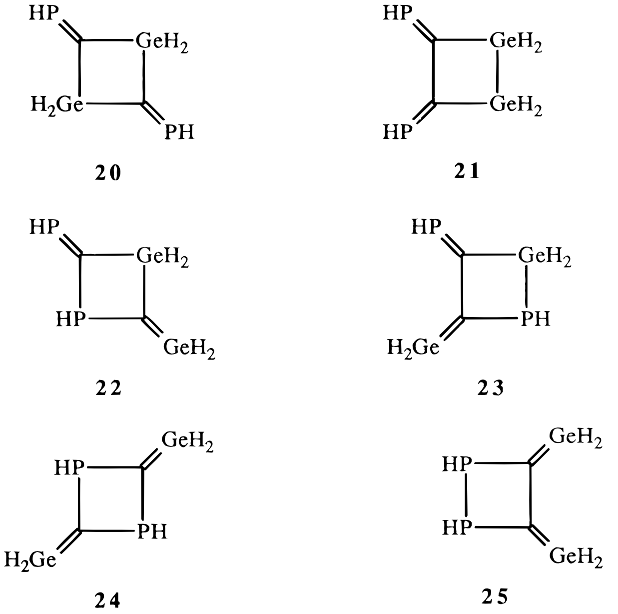
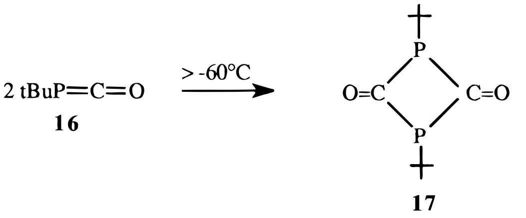
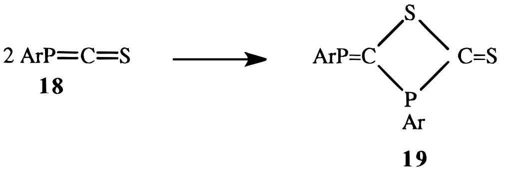
Chart 4



between two P=C bonds (eq 3), and phosphathioketene between one P=S and one C=S bond (eq 4).



3)



4)

However calculations on the dimerization of phosphaketene **16** have shown that the relative activation energies for the dimerization pathways involving two P=C bonds or one P=C and one C=O bond are sensitive to computational level and, thus, are close.[14]

Preliminary calculations[17−20] have been performed on model dimers **20**−**25** resulting from the couplings of the two molecules of germaphosphaallene $H_2Ge{=}C{=}PH$ (Chart 4).

Chart 5

The adducts **24** and **25** are found to be disfavored with respect to the adducts **22** and **23** by about 25 kcal/mol. **22** and **23** are in turn disfavored with respect to **20** and **21** by about 18 kcal/mol. The head-to-head products **21**, **23**, and **25** are significantly more stable than the head-to-tail dimers **20**, **22**, and **24**. The corresponding energy differences are calculated at 1, 6, and 5 kcal/mol for the three cases, respectively. Without ignoring the significant butadiene-type conjugation occurring in the head-to-head dimers, all these relative energies can be accounted for using mean bond energies.

In agreement with these theoretical results, dimers like **24** and **25** are not actually observed; only dimers like **20** and **22** are obtained. However, the arrangement **20**, predicted to be the most favorable, is only the minor product observed.

Although the calculations favor the head-to-head dimers **21** and **23** (probably due to the butadiene-type conjugation they undergo), it is not surprising that only the head-to-tail dimers **20** and **22** were experimentally observed, given our very bulky substituents.

The main difference between the theoretical conclusions on the model compounds and the experimental results on the substituted compounds bearing mesityl and tri-*tert*-butylphenyl groups is the ordering **22** < **20** whereas **14a** is preponderant over **13**. On the other hand, the calculations show very little difference in energy between the cis and the trans PH arrangements for **20**, which is in agreement with the cis−trans thermodynamic equilibrium observed for **13**.

Perhaps the most interesting result of this potential surface exploration is the apparently unexpected thermodynamic stability of the bicyclic derivatives **26** and **27**, which were calculated to lie 15 kcal/mol *below* **20** and **21**. The existence of such bicyclo frames is made possible here, owing to the large difference between the P−P, Ge−P, and Ge−Ge bond lengths (2.2−2.5 Å) and the C=C distance (1.34 Å). This dissymmetry allows a butterfly type arrangement, which relieves the cyclic strain that could at first be expected (Chart 5).

Experimental Section

General Experimental Considerations. All experiments were carried out in flame-dried glassware under an atmosphere of argon. Et_2O and THF were distilled from sodium/benzophenone prior to use. NMR spectra were recorded on the following spectrometers: ^1H, Bruker AC 80 (80.13 MHz) and Bruker AC 200 (200.13 MHz); ^{13}C, Bruker AC 200 (50.32 MHz) (reference: TMS); ^{19}F, Bruker AC 80 (75.39 MHz) (reference: CF_3COOH); ^{31}P, Bruker AC 80 (32.44 MHz) and Bruker AC 200 (80.01 MHz) (reference: H_3PO_4 85%). The NMR solvent was always $CDCl_3$. Melting points have been determined on a Leitz 350 apparatus. Mass spectra have been collected on a Hewlett-Packard 5989 A spectrometer by EI at 70 eV and on a Nermag R 10010 spectrometer by CI with CH_4 and referenced to ^{74}Ge and

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(17) Restricted Hartree−Fock calculations have been performed with the GAUSSIAN 92 package.[18] For carbon, phosphorus, and germanium atoms, effective core potentials were used.[19] For all atoms, the valence atomic basis sets consist of four Gaussian functions contracted to a double-ζ level and augmented by a polarization function. The geometries are optimized by using a gradient technique. For the sake of reproductibility, the total valence energy for **21** is calculated at −34.374 365 au.

(18) Gaussian 92, Revision E.3: Frisch, M. J.; Trucks, G. W.; Head-Gordon, M.; Gill, P. M. W.; Wong, M. W.; Foresman, J. B.; Johnson, B. G.; Schlegel, H. B.; Robb, M. A.; Replogle, E. S.; Gomperts, R.; Andres, J. L.; Raghavachari, K.; Binkley, J. S.; Gonzalez, C.; Martin, R. L.; Fox, D. J.; Defrees, D. J.; Baker, J.; Stewart, J. J. P.; Pople, J. A. Gaussian, Inc., Pittsburgh, PA, 1992.

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(20) A theoretical study of the potential energy surface at a higher level of theory is in progress. The full set of results including methodological details, all geometrical parameters, and correlation corrections will be published separately.

^{79}Br. Elemental analyses were performed by the “Service de Microanalyse de l’Ecole de Chimie de Toulouse”.

4 and **12** have been prepared according to the procedure of Bickelhaupt[8] respectively from $ArPCl_2$, $CHBr_3$, and BuLi or $ArPCl_2$, CHI_3, and BuLi at low temperature (−90 °C).

Synthesis of 7. A solution of 1.6 M *n*-BuLi in hexane (5.1 mL, 8.2 mmol) was slowly added (during 30 min) to a solution of **4** (3.68 g, 8.2 mmol) in 75 mL of Et_2O cooled at −90 °C. The reaction mixture was stirred for 1 h at −90 °C and then cooled at −120 °C; a suspension of Mes_2GeF_2 (2.86 g, 8.2 mmol) in 25 mL of Et_2O was added. After 1 h of stirring at −80 °C, the mixture was allowed to warm very slowly (overnight) to room temperature. The solvents were eliminated in vacuo, and the residue was dissolved in 50 mL of pentane; LiF was filtered out. Recrystallization from pentane at −20 °C afforded 2.10 g (35%) of white crystals of **7** (mp 163−165 °C).

^{1}H NMR: δ 1.34 (s, 9H, *p*-*t*-Bu), 1.46 (d, $^5J_{HP} = 0.4$ Hz, 18H, *o*-*t*-Bu), 2.27 (s, 6H, *p*-Me), 2.43 (d, $^5J_{HF} = 2.0$ Hz, 12H, *o*-Me), 6.84 (s, 4H, H aromatic Mes), 7.42 (d, $^4J_{PH} = 1.5$ Hz, 2H, H aromatic Ar). ^{31}P NMR: δ 321.3 (d, $^3J_{PF} = 29.8$ Hz). ^{19}F NMR: δ −97.6 (d, $^3J_{FP} = 29.8$ Hz). ^{13}C NMR: δ 21.18 (s, *p*-Me), 23.35 (d, $^4J_{CF} = 3.4$ Hz, *o*-Me), 31.36 (s, *p*-(CH_3)$_3$C), 33.16 (d, $^4J_{CP} = 7.1$ Hz, *o*-(CH_3)$_3$C), 35.06 (s, *p*-(CH_3)$_3$*C*), 37.99 (s, *o*-(CH_3)$_3$*C*), 122.39 (s, *m*-C Ar), 129.21 (s, *m*-C Mes), 133.09 (dd, $^3J_{CP} = 5.2$ Hz, $^2J_{CF} = 11.1$ Hz, C ipso Mes), 138.30 (d, $^1J_{CP} = 66.6$ Hz, C ipso Ar), 140.05 (s, *p*-C Mes), 143.15 (s, *o*-C Mes), 150.92 (s, *p*-C Ar), 153.09 (d, $^2J_{CP} = 2.2$ Hz, *o*-C Ar), 157.71 (dd, $^2J_{CF} = 10.4$ Hz, $^1J_{CP} = 86.6$ Hz, P=*C*Ge). MS EI (*m*/*z*): 697 (M − 1, 1); 683 (M − Me, 1); 641 (M − *t*-Bu, 1); 619 (M − Br, 2); 603 (M − Br − Me − 1, 1); 565 (M − Me − Mes + 1, 3); 331 (Mes_2GeF, 4); 311 (Mes_2Ge − 1, 3); 275 (ArP − 1, 8); 272 (MesGeBr, 1); 57 (*t*-Bu, 100). Anal. Calcd for $C_{37}H_{51}BrFGeP$: C, 63.64; H, 7.36. Found: C, 63.42; H, 7.20.

Characterization of 3. The reaction was carried out in a 10 mm diameter NMR tube in order to perform NMR studies at low temperature. To a solution of 0.25 g (0.36 mmol) of **7** in a mixture of THF-d_8 (1 mL) and toluene-d_8 (0.5 mL) cooled at −90 °C was added 1 equiv of 1.6 M *n*-BuLi in toluene-d_8 (0.7 mL) (hexane, solvent of *n*-BuLi, was removed in vacuo and replaced by toluene-d_8); the solution turned orange. A ^{31}P NMR spectrum showed the formation of the lithio compound **8**. When the reaction mixture was warmed between −70 and −40 °C, the germaphosphaallene **3** was formed and evidenced by ^{31}P NMR (δ: 239.7 ppm). After cooling of the sample at −80 °C to avoid dimerization of **3**, a ^{13}C NMR spectrum showed the signal of the allenic carbon at δ 280.93 ppm (d, $^1J_{CP} = 54.3$ Hz).

Synthesis of 11. A 8.5 mL portion of a solution of 1.6 M *n*-BuLi in hexane (13.7 mmol) was added dropwise to a solution of **12** (5.70 g, 13.7 mmol) in Et_2O (50 mL) cooled at −80 °C. After 10 min and then cooling at −120 °C, a suspension of Mes_2GeF_2 (4.50 g, 13.7 mmol) in Et_2O (30 mL) was slowly added under vigorous stirring. The reaction mixture (orange-yellow) was very slowly warmed to room temperature in 2 h. The solvents were eliminated in vacuo and replaced by 50 mL of pentane. LiI was filtered off. Crude **11** was recrystallized from pentane to afford 2.90 g (35%) of yellow crystals (mp 148−150 °C).

^{1}H NMR: δ 1.35 (s, 9H, *p*-*t*-Bu), 1.47 (s, 18H, *o*-*t*-Bu), 2.26 (s, 6H, *p*-Me), 2.38 (d, $^5J_{HF} = 1.6$ Hz, 12H, *o*-Me), 6.81 (s, 4H, H aromatic Mes), 7.39 (d, $^4J_{HP} = 1.2$ Hz, 2H, H aromatic Ar), 8.13 (dd, $^3J_{HF} = 2.9$ Hz, $^2J_{HP} = 24.7$ Hz, 1H, P=C*H*). ^{31}P NMR: δ 334.7 (dd, $^3J_{PF} = 32.0$ Hz, $^2J_{PH} = 24.8$ Hz). ^{19}F{^{1}H} NMR: δ −99.6 (d, $^3J_{FP} = 32.0$ Hz). ^{13}C NMR: δ 21.20 (s, *p*-Me), 23.26 (s, *o*-Me), 31.42(s, *p*-(CH_3)$_3$C), 33.96 (d, $^4J_{CP} = 7.9$ Hz, *o*-(CH_3)$_3$C), 35.00 (s, *p*-*C*(CH_3)$_3$), 38.25 (s, *o*-*C*(CH_3)$_3$), 122.05 (s, *m*-C Ar), 129.05 (s, *m*-C Mes) 139.68 (s, *p*-C Mes), 142.83 (s, *o*-C Mes), 149.82 (s, *p*-C Ar), 152.78 (s, *o*-C Ar), 169.87 (dd, $^1J_{CP} = 69.5$ Hz, $^2J_{CF} = 9.4$ Hz, P=*C*). MS EI (*m*/*z*): 619 (M − 1, 31); 605 (M − Me, 1); 563 (M − *t*-Bu, 83); 543 (M − *t*-Bu − F − 1, 10); 331 (Mes_2GeF, 37); 311 (Mes_2Ge − 1, 16); 275 (ArP − 1, 94); 57 (*t*-Bu, 100). Anal. Calcd for $C_{37}H_{52}FGeP$: C, 71.75; H, 8.46. Found: C, 71.41; H, 8.33.

Synthesis of 9. a. From 3. To a solution of 0.36 g (0.52 mmol) of **7** in Et_2O (2 mL) cooled at −90 °C was added 1 equiv of 1.6 M *n*-BuLi in hexane (0.33 mL); the solution turned orange. The reaction mixture was stirred for 15 min at -40 °C and then cooled at −80 °C, and a 2-fold excess of methanol was added; the reaction mixture turned from red to yellow. After removal of solvents, addition of pentane, and filtration, **9** was characterized by NMR. **9** was not obtained completely pure in this reaction, because trace amounts of **7** and **11** (hydrolysis of **8**) could not be removed. The yield of **9**, calculated from NMR, was 80%.

b. From 11. A solution of 1.6 M *n*-BuLi in hexane (0.53 mL, 0.85 mmol) was slowly added to 10 mL of MeOH. The resulting solution of MeOLi was added to a solution of **11** (0.53 g, 0.85 mmol) in Et_2O (20 mL) cooled at −78 °C. After warming of the solution to room temperature and removal of Et_2O, 30 mL of pentane was added. LiF was filtered out. Recrystallization of crude **9** from pentane at −30 °C afforded 0.45 g (85%) of white crystals (mp: 143−145 °C).

^{1}H NMR: δ 1.33 (s, 9H, *p*-*t*-Bu), 1.43 (d, $^5J_{HP} = 0.4$ Hz, 18H, *o*-*t*-Bu), 2.24 (s, 6H, *p*-Me), 2.32 (s, 12H, *o*-Me), 3.37 (s, 3H, OMe), 6.78 (s, 4H, H aromatic Mes), 7.36 (d, $^4J_{HP} = 1.1$ Hz, 2H, H aromatic Ar), 8.25 (d, $^2J_{HP} = 25.5$ Hz, 1H, P=CH). ^{31}P NMR (C_6D_6): δ 325.7 (d, $^2J_{PH} = 25.5$ Hz). ^{13}C NMR: δ 21.13 (s, *p*-Me), 23.45 (s, *o*-Me), 31.42 (s, *p*-(CH_3)$_3$C), 33.84 (d, $^4J_{CP} = 7.8$ Hz, *o*-(CH_3)$_3$C), 34.97 (s, *p*-*C*(CH_3)$_3$), 38.22 (s, *o*-*C*(CH_3)$_3$), 52.25 (s, OMe), 121.92 (s, *m*-C Ar), 128.83 (s, *m*-C Mes), 138.81 (s, *p*-C Mes), 143.14 (s, *o*-C Mes), 149.39 (s, *p*-C Ar), 152.74 (s, *o*-C Ar), 172.23 (d, $^1J_{CP} = 71.3$ Hz, P=*C*). MS EI (*m*/*z*): 632 (M, 8); 575 (M − *t*-Bu, 5); 545 (M − *t*-Bu − OMe + 1, 6); 343 (Mes_2GeOMe, 69); 275 (ArP − 1, 57); 193 (MesGe, 16); 179 (MesGe − Me + 1, 25); 57 (*t*-Bu, 100). Anal. Calcd for $C_{38}H_{55}OGeP$: C, 72.28; H, 8.78. Found: C, 72.39; H, 8.70.

Synthesis of 10. a. From 3. The procedure was exactly the same as previously described for **9**. Addition of MeLi (2 equiv) at −80 °C to **3** caused a change from red to orange yellow. After warming of the solution to room temperature, a slight excess of methanol was added. After the usual workup, **10**, with some amounts of **7** and **11**, was obtained. The NMR yield was 75%. Pure **10** could be obtained from **11**.

b. From 11. To a solution of **11** (0.53 g, 0.85 mmol) in Et_2O (10 mL) cooled at −78 °C was added dropwise 1 equiv of 1.6 M MeLi in hexane. After being warmed to room temperature, the reaction mixture was heated for 1 h at reflux. After the usual workup (elimination of Et_2O, addition of pentane, filtration), recrystallization from pentane gave 0.42 g (80%) of white crystals of **10** (mp 74−76 °C).

^{1}H NMR: δ 1.03 (d, $^4J_{HP} = 0.9$ Hz, 3H, GeMe), 1.33 (s, 9H, *p*-*t*-Bu), 1.40 (d, $^5J_{HP} = 0.5$ Hz, 18H, *o*-*t*-Bu) 2.24 (s, 18H, *o*- and *p*-Me), 6.74 (s, 4H, H aromatic Mes), 7.35 (d, $^4J_{HP} = 1.1$ Hz, 2H, H aromatic Ar), 8.37 (d, $^2J_{HP} = 26.3$ Hz, 1H, P═C*H*). ^{31}P NMR (C_6D_6): δ 310.8 (d, $^2J_{PH} = 26.3$ Hz). ^{13}C NMR: δ 5.59 (d, $^3J_{CP} = 12.0$ Hz, MeGe), 21.06 (s, *p*-Me), 24.24 (s, *o*-Me), 31.44 (s, *p*-(CH$_3$)$_3$C), 33.79 (d, $^4J_{CP} = 7.7$ Hz, *o*-(CH$_3$)$_3$C), 34.96 (s, *p*-C(CH$_3$)$_3$), 38.26 (s, *o*-C(CH$_3$)$_3$), 121.87 (s, *m*-C Ar), 128.80 (s, *m*-C Mes), 137.22 (d, $^3J_{CP} = 6.7$ Hz, C ipso Mes), 137.76 (s, *p*-C Mes), 142.41 (s, *o*-C Mes), 149.14 (s, *p*-C Ar), 152.67 (s, *o*-C Ar), 177.59 (d, $^1J_{CP} = 71.9$ Hz, P═*C*). MS (*m*/*z*): 616 (M, 3); 559 (M − *t*-Bu, 26); 543 (M − *t*-Bu − Me − 1, 1); 439 (M − *t*-Bu − Mes − 1, 15); 327 (Mes_2GeMe, 16); 276 (ArP, 15); 275 (ArP − 1, 69); 207 (MesGeMe − 1, 20); 193 (MesGe, 23); 57 (*t*-Bu, 100). Anal. Calcd for $C_{38}H_{55}GeP$: C, 74.16; H, 9.01. Found: C, 74.06; H, 9.01.

Synthesis of Dimers 14a and 13a. A solution of 1.6 M *n*-BuLi in hexane (2.2 mL, 3.5 mmol) was slowly added to a solution of **7** (2.42 g, 3.5 mmol) in Et_2O (20 mL) cooled at −80 °C; the reaction mixture turned orange yellow and was stirred for 15 min. During the warming to room temperature, the mixture gradually turned red and then dark red. **13a**, almost insoluble in Et_2O, could be isolated by filtration and was recrystallized from $CHCl_3$. Et_2O was eliminated from the solution containing **14a**. A 50 mL portion of pentane was added, and LiF was filtered off. ^{31}P NMR spectrum of the solution showed the formation of **14a**. **14a**, with a reactive Ge═C double bond, could not be obtained in pure form.

14a: ^{31}P NMR (C_6D_6) AX system, δ_A 269.5 (d, $^2J_{PP} = 225.4$ Hz, P═C), δ_X 61.3 (d, $^2J_{PP} = 225.4$ Hz, P−C). **13a**: 0.20 g, Rdt = 10%, mp 290 °C, dec. ^{1}H NMR: δ 1.04 (s, 18H, *o*-*t*-Bu), 1.30 (s, 9H, *p*-*t*-Bu), 2.08 (s, 12H, *o*-Me), 2.15 (s, 6H, *p*-Me), 6.51(s, 4H, H aromatic Mes), 7.04 (broad signal, 2H, H aromatic Ar). ^{31}P NMR (C_6D_6): δ 381.0. ^{13}C NMR: δ 20.85 (s, *p*-Me), 25.36 (s, *o*-Me), 31.47 (s, p-(CH$_3$)$_3$C), 33.85 (s, *o*-(CH$_3$)$_3$C), 34.74 (s, *p*-C(CH$_3$)$_3$), 38.42 (s, *o*-C(CH$_3$)$_3$), 122.08 (s, *m*-C Mes), 128.34 (s, *m*-C Ar), 137.17 (s, *p*-C Mes), 142.34 (s, *o*-C Mes), 148.51 (s, *p*-C Ar), 152.89 (s, *o*-C Ar). MS CI (CH_4) (*m*/*z*): 1199 (M + 1); 1183 (M − Me, 15); 1080 (M − Mes + 1, 43); 1023 (M − Mes − *t*-Bu + 1, 22); 953 (M − Ar, 100). Anal. Calcd for $C_{74}H_{102}Ge_2P_2$: C, 74.14; H, 8.58. Found: C, 74.01; H, 8.38.

Synthesis of 15. To a dark red solution of **14a** (2.03 mmol) prepared as previously described was added an excess of 1.6 M MeLi in Et_2O (2.5 mL, 4.06 mmol). The reaction mixture was heated at reflux for 30 min and turned purple. Methanol (4.06 mmol) in pentane (10 mL) and then an excess of methyl iodide were successively added. After elimination of Et_2O in vacuo, 30 mL of pentane was added. Lithium salts were filtered out. **15** was isolated in the form of a purple powder: 2.00 g (80%, mp 148−150 °C).

^{31}P NMR: AX system, δ_A 352.6 (d, $^2J_{PP} = 112.9$ Hz, P═C), δ_X 31.9 (d, $^2J_{PP} = 112.9$ Hz, P−C). ^{1}H NMR: δ 1.14 (d, $^4J_{HP} = 0.7$ Hz, 3H, CH_3Ge); 1.26−1.45 (m, 27H, *t*-Bu); 1.88−2.37 (m, 18H, *o*- and *p*-Me); 6.42−7.41 (m, 6H, H aromatic Mes and H aromatic Ar). ^{13}C NMR: δ 13.53 (s, CH_3Ge); 21.07 (s, *p*-CH_3); 23.76, 24.32, 24.48, 24.78, 24.95 (*o*- + *p*-CH_3); 31.67 (s, *p*-(CH$_3$)$_3$C); 33.76, 33.99, 34.11 (broad s, *o*-(CH$_3$)$_3$C); 29.89, 35.14 (s, *p*-(CH$_3$)$_3$$C$); 38.56 (d, *o*-(CH$_3$)$_3$$C$, $^3J_{CP} = 4.5$ Hz); 121.93, 122.49 (*m*-C Ar) 128.37, 128.80, 128.92, 128.99, 129.30 (*m*-C Mes); 136.45, 136.88, 137.06, 137.22 (*p*-C Mes); 142.16, 142.45, 142.86, 142.91 (*o*-C Mes); 149.52, 150.06 (*p*-C Ar); 153.83, 154.32 (*o*-C Ar). MS EI (*m*/*z*): 1042 (M − 3*t*-Bu − 1, 1); 1025 (M − C_6H_2*t*-Bu_2 − 1, 2); 983 [M − Ar′ + 1 (Ar′ = Ar − Me), 3]; 953 (M − Ar − Me − H, 1); 888 (M − Mes_2GeMe + 1, 1); 851 (M − Mes − Ar + 1, 1); 600 ($Mes_2Ge{=}C{=}PAr$, 3); 430 ($Mes_2Ge{=}C{=}PAr$ − 3*t*-Bu + 1, 3); 327 (Mes_2GeMe, 15); 57 (*t*-Bu, 100). Anal. Calcd for $C_{75}H_{106}Ge_2P_2$: C, 74.15; H, 8.80. Found: C, 73.88; H, 8.51.

Isolation of 13a,b. After some days at room temperature, a solution of **13a** in Et_2O or $CHCl_3$ gave a mixture of **13a**,**b**.

13a is very slightly soluble in pentane whereas **13b** is fairly soluble. Thus, addition of pentane to a mixture of **13a**/**13b** solubilizes **13b**: filtration affords solid **13a**, whereas **13b** is obtained after removal of solvent from the filtrate.

13b: ^{1}H NMR δ 1.05 (s, 18H, *o*-*t*-Bu); 1.26 (s, 9H, *p*-*t*-Bu); 1.55 (s, 6H, *o*-Me cis to Ar rings); 2.10 (s, 3H, *p*-Me cis to Ar rings); 2.24 (s, 3H, *p*-Me cis to lone pairs); 2.51 (s, 6H, *o*-Me cis to lone pairs); 6.35 (s, 2H, H aromatic Mes cis to Ar rings); 6.75 (s, 2H, H aromatic Mes cis to lone pairs); 7.02 (s, 2H, H aromatic Ar).

13b: ^{31}P NMR δ 374.7 ppm.

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