ELSEVIER

Journal of Organometallic Chemistry 643–644 (2002) 202–208

Journal of Organometallic Chemistry

www.elsevier.com/locate/jorganchem

The first stable 3,1-germaphosphaallene Tip(t-Bu)Ge=C=PAr

Yamna El Harouch, Heinz Gornitzka, Henri Ranaivonjatovo, Jean Escudié *

Hétérochimie Fondamentale et Appliquée, UMR 5069, Université P. Sabatier, 118 route de Narbonne, 31062 Toulouse Cedex 04, France

Received 29 June 2001; accepted 5 September 2001

Dedicated to Professor François Mathey on the occasion of his 60th birthday

---

Abstract

The first stable heteroallenic derivative with two heavy doubly-bonded Group 14 and 15 elements, the germaphosphaallene Tip(t-Bu)Ge=C=PAr **1** (Tip = 2,4,6-triisopropylphenyl, Ar = 2,4,6-tri-*tert*-butylphenyl), has been prepared in a nearly quantitative yield by dechlorofluorination of Tip(t-Bu)Ge(F)–C(Cl)=PAr (obtained from ArP=CCl_2 and successive reaction with n-butyllithium and Tip(t-Bu)GeF_2) with *tert*-butyllithium. **1** gives [2 + 2] cycloadducts by the Ge=C double bond with benzaldehyde, benzophenone and fluorenone to afford the corresponding germaoxetanes **11**–**13**. **13** has been structurally characterized showing a long Ge–O bond (1.821(2) Å) and a slightly folded four-membered ring GeOCC (18.8° along C(1)Ge axis). © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Germaphosphaallene; Doubly-bonded derivatives of germanium and phosphorus; [2 + 2] Cycloadditions; Germaoxetanes

---

1. Introduction

As almost all the possible combinations of E=E′ compounds (E, E′ = Group 14, 15 and 16 elements) have been reported in the literature over the last 20 years, an exciting challenge was now the synthesis and the stabilization of compounds with two cumulative double bonds of the type E=C=E′. Many heteroallenes of heavy Group 15 elements such as –P=C=E′ (E′ = C, N, P, As, O, S) have now been described [1,2]. By contrast, heteroallenes with at least one heavy Group 14 element are much more rare [2,3] since in the field of >E=C=E′ derivatives (E = Si, Ge, Sn; E′ = C, N, P, O) only some 1-silaallenes >Si=C=C< [4] and 1-germaallenes >Ge=C=C< [5] have been isolated and some transient 1-silaallenes spectroscopically characterized [6].

By contrast with the >E=C=C< derivatives which keep their ECC skeleton in trapping reactions, SiCO [7], SiCN [8] and SnCN [9] derivatives have a very labile Si (or Sn)–C bond and they can be better described as silylene-CO adducts and silylenes (or stannylene)-isocyanide adducts rather than heteroallenes.

In the field of E=C=E′ derivatives, with two heavy elements of Groups 14 and 15, no stable compounds could be obtained until now. The only ones to be reported were the 3,1-phosphasilaallene Tip(Ph)Si=C=PAr (Tip = 2,4,6-i-$Pr_3C_6H_2$; Ar = 2,4,6-t-$Bu_3C_6H_2$) [10] and the 3,1-germaphosphaallene Mes_2Ge=C=PAr (Mes = 2,4,6-$Me_3C_6H_2$) [11] which have been evidenced by NMR and by trapping reactions at low temperature. Due to their very low thermal stability, dimerization occurs rapidly above −40 °C. However, such compounds keep their structural integrity in solution and their bonding is closer to those of metallaallenes >E=C=C< than those of SiCO and Si (or Sn) CN compounds.

We describe in this paper the synthesis, the physicochemical study and some preliminary aspects of the reactivity of the 3-(2,4,6-triisopropylphenyl)-3-*tert*-butyl-1-(2,4,6-tri-*tert*-butylphenyl)-3-germa-1-phosphaallene **1**, which is the first heteroallenic derivative with two heavy doubly-bonded Group 14 and 15 elements stabilized at room temperature owing to bulky groups on germanium and phosphorus.

---

* Corresponding author. Tel.: +33-5-61558347; fax: +33-5-61558204.

E-mail address: escudie@chimie.ups-tlse.fr (J. Escudié).

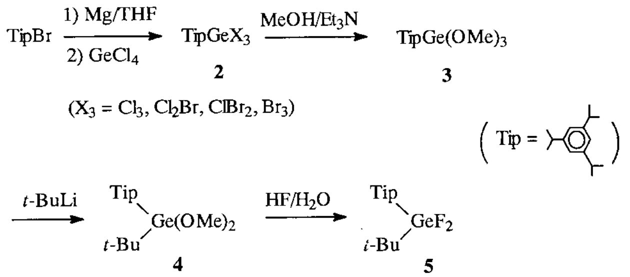
PII: S0022-328X(01)01223-2

2. Results and discussion

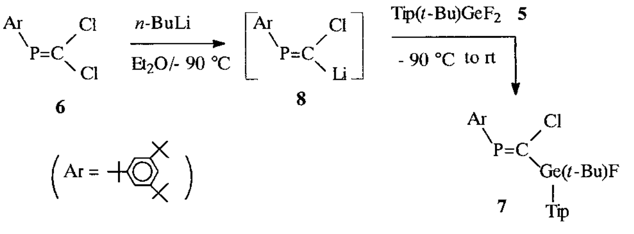
2.1. Synthesis of **1**

As the Ge=C double bond was supposed to be much more reactive than the P=C double bond, the creation of this Ge=C unsaturation was the final step of the synthesis.

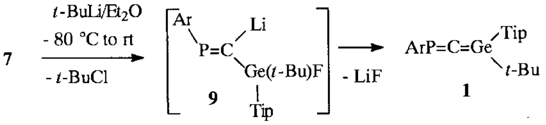
From TipBr, **2** is obtained as a mixture of chloro- and bromogermanes which can be converted to the corresponding trimethoxygermane **3** without purification. Addition of *tert*-butyllithium to **3** afforded the dimethoxygermane **4**. The difluorogermane **5** was then prepared by reaction with hydrofluoric acid in water (Scheme 1).



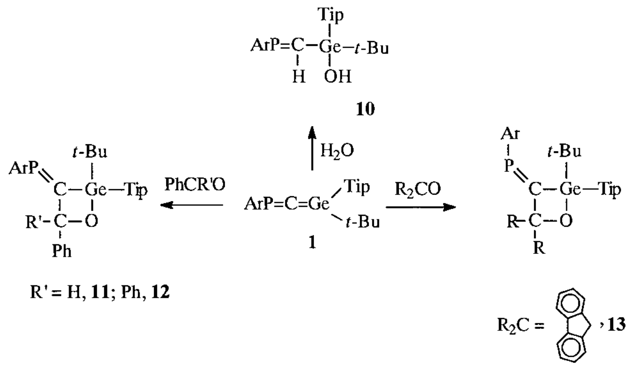
Scheme 1.



Scheme 2.



Scheme 3.



Scheme 4.

Starting from the dichlorophosphaalkene **6** [12], the germylphosphaalkene **7** was prepared by successive addition of *n*-butyllithium at low temperature and difluorogermane **5** (Scheme 2).

Compound **7** was obtained in the form of only one isomer. We suggest it is the *Z* isomer from the most probable mechanism supposed to occur, involving a halogen–metal exchange with *n*-butyllithium from the least hindered side, i.e. the *E*-chlorine, to give the transient carbenoid **8**. Such a stereochemistry was previously reported [13].

The great steric hindrance occurring in **7** was clearly evidenced in its ^{1}H-NMR spectrum: two signals for the *o*-*t*-Bu groups and a very broad signal for the methyls of *o*-$CHMe_2$ groups were observed due to the hindered rotation of the Ar and Tip groups.

Addition of one equivalent of *tert*-butyllithium at − 90 °C led nearly quantitatively to the germaphosphaallene **1** probably via the intermediate **9** (Scheme 3).

Unfortunately, the obtaining of a single crystal suitable for an X-ray determination failed. However, the NMR studies proved unambiguously the allenic structure of **1**. The ^{13}C chemical shift for the carbon bonded to germanium and phosphorus (280.4 ppm, $^{1}J_{PC} = 60.9$ Hz) is characteristic of an allenic carbon [1–3] (for example: 280.9 ppm in ArP=C=$GeMes_2$ [11], 299.5 ppm in ArP=C=AsAr [14], 269.1 ppm in Tip(Ph)Si=C=PAr [10], 235.1 in Tip_2Ge=C=C(Ph)*t*-Bu [5c] and 243.5 in Tbt(Mes)Ge=C=CR_2 (CR_2 = fluorenylidene, Tbt = 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl) [5b]). The low-field chemical shift in ^{31}P-NMR (249.9 ppm) is also consistent with the assigned structure (δ ^{31}P: 240 ppm in Mes_2Ge=C=PAr [11]).

The germaphosphaallene **1** is the first stable allenic compound with two heavy Group 14 and 15 elements. Orange solutions of **1** in pentane or toluene are extremely air and moisture sensitive but under inert atmosphere, they are recovered unchanged after at least 2 weeks at room temperature.

1 presents a chemical behaviour rather different from that of the two transient metallaphosphaallenes previously described, the germaphosphaallene Mes_2Ge=C=PAr [11] and the phosphasilaallene Tip(Ph)Si=C=PAr [10] which give two types of dimers, a head-to-tail dimer by two M=C bonds (M = Si, Ge) and an unsymmetrical dimer by one M=C and one P=C bonds above − 40 °C.

2.2. Reactivity of **1**

Water adds regiospecifically to the Ge=C unsaturation of **1** to give the corresponding adduct **10** with the hydroxy moiety bonded as expected to the germanium due to the $Ge^{\delta+}$–$C^{\delta-}$ polarity (Scheme 4). It has not

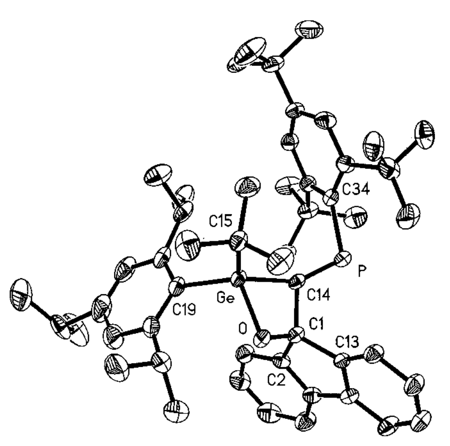


Fig. 1. Molecular structure of **13**. Ellipsoids are drawn at 50% probability level. Hydrogen atoms and the molecule of $CHCl_3$ are omitted for clarity.

Table 1
Selected bond lengths (Å), bond angles (°) and torsion angles (°) in germaoxetane (**13**)

Bond lengths	
C(1)–O	1.450(4)
Ge–O	1.826(2)
C(1)–C(14)	1.552(5)
Ge–C(14)	2.003(3)
C(1)–C(2)	1.531(5)
C(1)–C(13)	1.526(4)
Ge–C(15)	1.983(3)
Ge–C(19)	1.981(3)
P–C(14)	1.661(4)
P–C(34)	1.853(3)
Bond angles	
O–Ge–C(14)	74.07(12)
Ge–O–C(1)	96.09(18)
O–C(1)–C(14)	100.6(2)
C(1)–C(14)–Ge	86.1(2)
Ge–C(14)–P	152.70(19)
C(1)–C(14)–P	119.3(2)
C(14)–P–C(34)	106.74(16)
C(15)–Ge–C(19)	114.97(14)
O–Ge–C(19)	105.65(13)
C(14)–Ge–C(15)	118.01(13)

Distances to the mean plane C(1)–C(14)–O–Ge: C(1): +0.1144 Å; C(14): −0.0847 Å, O: −0.1004 Å, Ge: +0.0706 Å.

been possible from the P–H coupling constant (25.0 Hz) to determine its stereochemistry *Z* or *E* by comparison with the literature data on the similar C-germylphosphaalkene ArP=C(H)$GeMe_3$ [12]; the latter displays $^2J_{PH}$ constants of respectively 26.4 Hz for the *E* and 23.5 Hz for the *Z* isomer [12], both close to the constant determined in **10**.

Aldehydes such as benzaldehyde and ketones such as benzophenone and fluorenone react with the Ge=C double bond of **1** to give [2+2] cycloadducts. The germaoxetanes **11–13** are air and moisture stable and are the first germaoxetanes with an exocyclic double bond. In heterocycle **11** formed from benzaldehyde, as germanium and the carbon bonded to oxygen are chiral, two diastereoisomers are obtained as expected in the ratio 65/35. In the three germaoxetanes **11–13** only one geometric isomer was obtained relatively to the exocyclic P=C double bond. The X-ray study of **13** shows it is the *Z*-isomer; although **13**-*Z* is the most hindered isomer, its formation can be easily explained since it arises from the preferential addition of fluorenone to the less hindered side of the Ge=C double bond, i.e. in *cis* to the lone pair of phosphorus. Thus, the Ar and Ge(*t*-Bu)Tip groups are in *cis* position. We suppose to obtain the same stereochemistry in **11** and **12**.

In the reaction of the silaallene Tip_2Si=C=C(*t*-Bu)Ph with benzophenone, [4c] West observed the formation of a four-membered ring silaoxetane (cycloaddition between Si=C and C=O double bonds) and the presence as major compound, like in our case, of the more hindered isomer (Si and *t*-Bu groups in *cis*). However, due to a lower difference of steric hindrance between *t*-Bu and phenyl groups, he obtained also the other isomer in a minor ratio.

The great difference in size between Ar and the phosphorus lone pair explains the formation of the sole **13**-*Z*.

The structure of the germaoxetane **13** has been proved by an X-ray crystallographic analysis (Fig. 1 and Tables 1 and 2).

The four-membered ring is slightly folded: the angles between the C(1)OGe and C(1)C(14)Ge planes is 18.9° and between OC(1)C(14) and OGeC(14) 18.7°. A similar folding was determined in other 2-germaoxetanes [15] and 2-silaoxetanes [16]. It is greater than the folding in 1,3-digermaoxetanes [17] but less important than the one reported in 1,3-digermazanes [18].

The Ge–O bond length (1.826(2) Å) is somewhat longer than the standard corresponding bond (standard range: 1.73–1.80 Å) [19,20] and is comparable to the one measured in other germaoxetanes with the germanium atom substituted by bulky groups [15]. However, a longer Ge–O bond length (1.872(4) Å) has been reported in an extremely congested oxazagermete ring system [21]. The Ge–C bond in the four-membered ring (2.003(3) Å) is also rather long (normal Ge–C distances are generally between 1.90 and 2.00 Å [20,22]). The small angle of 74.07(12)° at the germanium atom is not unusual; similar values have been reported in other four-membered ring derivatives of germanium: for example 74.1° in a 3,4-digerma-1,2-dioxetane [17], 75.0 in a 2-germaphosphetene [23], 75(1) and 75.6(2) in 2-germaoxetanes [15]. The carbon atom of the C=P double bond is almost planar (sum of angles: 358.1°). The exocyclic C=P bond is slightly twisted with a twist angle of 10.5° between the C(1)C(14)Ge and C(14)PC(33) planes. The bond lengths and bond angles within the Tip, Ar and fluorenyl groups span the normal limits.

In conclusion, the title germaphosphaallene is the first compound of this type stable as a monomer. Despite the great steric hindrance necessary for its stabilization, it presents a very reactive Ge=C double bond towards water or carbonyl compounds, while the P=C double bond is inert in these reactions. The intensive study of the chemical behavior of such a derivative is under investigation.

3. Experimental

All reactions were carried out under N_2 or Ar with carefully dried solvents. NMR spectra were recorded on Bruker AC 80, AC 200 and AC 250 at the respective frequencies (^1H: 80.13, 200.13 and 250.13 MHz), ^{13}C (50.323 and 62.896 MHz), ^{19}F (ref. CF_3COOH, 188.298 MHz) and ^{31}P (ref. H_3PO_4, 81.015 MHz); when no NMR solvent is mentioned, it was $CDCl_3$. Mass spectra were obtained from a Hewlett–Packard HP 5989 spectrometer in the electron-impact mode (70 eV). Melting points (m.p.) were measured on a Leitz microscope.

Table 2
Crystal data and structure refinement parameters for compound **13**

Empirical formula	$C_{51}H_{69}GeOP \cdot CHCl_3$
Formula weight	920.99
Temperature (K)	193(2)
Wavelength (Å)	0.71073
Crystal system	Triclinic
Space group	$P\bar{1}$
a (Å)	10.1917(8)
b (Å)	13.4654(11)
c (Å)	19.1643(15)
α (°)	82.962(2)
β (°)	83.578(2)
γ (°)	72.0340(10)
V (Å^3)	2475.3(3)
Z	2
D_{calc} (Mg m^{-3})	1.236
Absorption coefficient (mm^{-1})	0.848
$F(000)$	976
Crystal size (mm)	$0.3 \times 0.5 \times 0.6$
Theta range for data collection (°)	1.60–24.71
Index ranges	$-11 \leq h \leq 11$, $-15 \leq k \leq 15$, $22 \leq l \leq 22$
Reflections collected	12 153
Independent reflections	8342 [$R_{int} = 0.0471$]
Completeness to $\theta = 26.37°$	98.7%
Absorption correction	None
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	8342/158/596
Goodness-of-fit on F^2	0.981
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0489$, $wR_2 = 0.1288$
R indices (all data)	$R_1 = 0.0683$, $wR_2 = 0.1366$
Largest difference peak and hole (e Å^{-3})	0.474 and -0.720

3.1. *2,4,6-Triisopropylphenyl(trimethoxy)germane (**3**)*

To a solution of $TipGeCl_3$ (4.64 g, 12.0 mmol) in toluene (40 ml) were added 15 ml of CH_3OH and 10 ml of triethylamine. The reaction mixture was refluxed for 1 h. After warming to room temperature (r.t.), the solvents were removed in vacuo and 100 ml of pentane were added. $Et_3N \cdot HCl$ was filtered out. After removal of pentane, 3.92 g (87%) of **3** were obtained as a viscous oil.

^1H-NMR: δ 1.24 (d, $^3J_{HH} = 6.7$ Hz, 18H, *o* and *p*-CH*Me*$_2$); 2.87 (sept, $^3J_{HH} = 6.7$ Hz, 1H, *p*-CH*Me*$_2$); 3.41 (sept, $^3J_{HH} = 6.7$ Hz, 2H, *o*-C*H*Me$_2$); 3.67 (s, 9H, OMe); 7.08 (s, 2H, arom H). Anal. Found: C, 58.79; H, 8.92. Calc. for $C_{18}H_{32}GeO_3$: C, 58.58; H, 8.74%.

3.2. *2,4,6-Triisopropylphenyl(tert-butyl)dimethoxygermane (**4**)*

A solution of *tert*-butyllithium 1.6 M in pentane (5 ml, 7.8 mmol) was slowly added to a solution of **3** (2.80 g, 7.60 mmol) in pentane (30 ml) cooled to 0 °C. After the end of the addition, the reaction mixture was refluxed for 1 h, then cooled to r.t.; 1 ml of methyl iodide (to transform MeOLi to LiI and Me_2O) was added and LiI was filtered out. Crystallization from pentane afforded 2.25 g of white crystals of **4** (75%), m.p. 112 °C.

^1H-NMR: δ 1.18 (s, 9H, CMe_3); 1.24 (d, $^3J_{HH} = 7.0$ Hz, 18H, *o* and *p*-CH*Me*$_2$); 2.86 (sept, $^3J_{HH} = 6.9$ Hz, 1H, *p*-C*H*Me$_2$); 3.39 (sept, $^3J_{HH} = 6.7$ Hz, 2H, *o*-C*H*Me$_2$); 3.65 (s, 6H, OMe); 7.05 (s, 2H, arom H).

^{13}C-NMR: δ 23.83 (*p*-CH*Me*$_2$); 25.78 (*o*-CH*Me*$_2$); 27.62 (C*Me*$_3$); 29.72 (*C*Me$_3$); 34.08 (*o* and *p*-*C*HMe$_2$); 53.05 (OMe); 122.17 (*m*-CH Tip); 126.80 (*ipso*-C Tip); 150.56 (*p*-C Tip); 155.93 (*o*-C Tip).

MS: 364 [M − OMe − H, 33]; 339 [M − *t*-Bu, 48]; 333 [M − 2OMe − 1, 2]; 307 [M − *t*-Bu − OMe − 1, 47]; 275 [M − 2OMe − *t*-Bu − 2, 100]; 57 (*t*-Bu, 97).

Anal. Found: C, 64.04; H, 9.78. Calc. for $C_{21}H_{38}GeO_2$: C, 63.84; H, 9.69%.

3.3. *Difluoro(2,4,6-triisopropylphenyl)(tert-butyl)germane (**5**)*

To a solution of **4** (1.52 g, 3.8 mmol) in 15 ml of C_6H_6 was added a solution at 40% of HF in H_2O (5 ml, large excess). After 1 h at reflux, the two layers were separated. The aq. layer was extracted with Et_2O. After drying over Na_2SO_4 and removal of solvents in vacuo, crude **5** was crystallized from pentane to give 1.12 g (78%) of white crystals. m.p. 104–106 °C.

^1H-NMR: δ 1.24 (d, $^3J_{HH} = 6.8$ Hz, 6H, *p*-CH*Me*$_2$); 1.28 (t, $^4J_{HF} = 1.6$ Hz, 9H, CMe_3); 1.28 (d, $^3J_{HH} = 6.8$ Hz, 12H, *o*-CH*Me*$_2$); 2.88 (t, sept, $^3J_{HH} = 6.8$ Hz, $^5J_{HF} = 2.2$ Hz, 2H, *o*-C*H*Me$_2$); 2.94 (sept, $^3J_{HH} = 6.8$ Hz, 1H, *p*-C*H*Me$_2$); 7.09 (s, 2H, arom H).

^{13}C-NMR: δ 23.81 (*p*-CH*Me*$_2$); 25.21 (*o*-CH*Me*$_2$); 25.94 (C*Me*$_3$); 34.39 (*p*-*C*HMe$_2$); 36.22 (t, $^5J_{CF} = 3.2$ Hz, *o*-*C*HMe$_2$); 122.46 (*m*-CH Tip); 152.74 (*p*-C Tip); 155.27 (*o*-C Tip). ^{19}F-NMR: δ -83.7 ppm.

MS: 372 [M, 6]; 352 [M − F − 1, 2]; 316 [M − *t*-Bu + 1, 12]; 295 [M − F − *t*-Bu − 1, 20]; 277 [M − 2F − *t*-Bu, 15]; 203 (Tip, 30); 27 (*t*-Bu, 100).

Anal. Found: C, 61.58; H, 8.91. Calc. for $C_{19}H_{32}F_2Ge$: C, 61.50; H, 8.69%.

3.4. Synthesis of **7**

A solution of ArP=CCl$_2$ [12] (2.83 g, 7.8 mmol) in THF (60 ml) was cooled to −90 °C. A solution of *n*-butyllithium 1.6 M in hexane (5.2 ml, 8 mmol) was slowly added at −90 °C then the reaction mixture was stirred for 30 min at −70 °C. A solution of **5** (2.92 g, 7.8 mmol) in THF (60 ml) was added at this temperature. After 30 min at −70 °C, the reaction mixture was allowed to warm to r.t. Solvents were evaporated in vacuo, 100 ml of pentane were added and LiF was removed by filtration. Crystallization from pentane gave 2.15 g of **7** (41%), m.p. 142–144 °C.

^{1}H-NMR: δ 1.23 (d, $^3J_{HH} = 6.8$ Hz, 18H, *o* and *p*-CH*Me*$_2$); 1.31 (s, 9H, *p*-CMe$_3$); 1.37 (d, $^4J_{HF} = 1.4$ Hz, 9H, GeCMe$_3$); 1.47 (d, $^5J_{HP} = 0.5$ Hz, 9H, *o*-CMe$_3$); 1.51 (d, $^5J_{HP} = 0.7$ Hz, 9H, *o*-CMe$_3$); 2.86 (sept, $^3J_{HH} = 6.8$ Hz, 3H, *o* and *p*-C*H*Me$_2$); 7.04 (s, 2H, arom H Tip); 7.39 (d, $^4J_{HP} = 1.5$ Hz, 2H, arom H Ar).

^{13}C-NMR: δ 23.85 (*p*-CH*Me*$_2$); 26.49 (*o*-CH*Me*$_2$); 28.3 (d, $^3J_{CF} = 4.5$ Hz, GeC*Me*$_3$); 32.08 (d, $^2J_{CF} = 10.5$ Hz, Ge*C*Me$_3$); 32.81, 32.95, 33.10, 34.08 (*o* and *p*-*C*HMe$_2$); 35.08 (*p*-*C*Me$_3$); 37.87 (d, $^3J_{CP} = 6.6$ Hz, *o*-*C*Me$_3$); 121.73, 122.30 (*m*-CH Ar and Tip); 127.41 (d, $^2J_{CF} = 6.5$ Hz, *ipso*-C Tip); 134.41 (d, $^1J_{CP} = 65.4$ Hz, *ipso*-C Ar); 150.72 (*p*-C Tip and *p*-C Ar); 153.18 (d, $^3J_{CF} = 2.3$ Hz, *o*-C Ar); 156.70 (*o*-C Tip); 169.31 (dd, $^1J_{CP} = 88.4$ Hz, $^2J_{CF} = 9.5$ Hz, P=C–Cl).

^{19}F-NMR: δ −103.2 ppm (d, $^3J_{FP} = 30.5$ Hz).

^{31}P-NMR: δ 297.6 ppm (d, $^3J_{PF} = 30.5$ Hz).

MS: 675 [M − 1, 1]; 657 [M − F, 1]; 641 [M − Cl, 2]; 633 [M − *i*-Pr, 4]; 619 [M − *t*-Bu, 11]; 600 [M − *t*-Bu − F, 2]; 577 [M − *i*-Pr − *t*-Bu + 1, 7]; 324 (ArP − CCl + 1, 11); 287 (ArP=C − 1, 40); 275 (ArP − 1, 27); 203 (Tip, 9); 57 (*t*-Bu, 100).

Anal. Found: C, 67.58; H, 9.17. Calc. For $C_{38}H_{61}ClFGeP$: C, 67.53; H, 9.10%.

3.5. 3-(2,4,6-triisopropylphenyl)-3-tert-butyl-1-(2,4,6-tri-tert-butylphenyl)germaphosphaallene (**1**)

To a solution of **7** (1.04 g, 1.54 mmol) in carefully deoxygenated and dried Et$_2$O cooled to −70 °C was added one equivalent of a solution of *tert*-butyllithium 1.6 M in pentane (1.1 ml). The solution became immediately red. After warming to r.t., LiF was filtered out giving a red-orange solution. A ^{31}P-NMR analysis showed the nearly quantitative formation of the germaphosphaallene **1**. Solutions of **1** can be used directly without further purification. After removal of solvents in vacuo, C$_6$D$_6$ was added to the crude crystalline product for NMR.

^{1}H-NMR (C$_6$D$_6$): δ 0.99, 1.24, 1.43 and 1.51 (4d, $^3J_{HH} = 6.8$ Hz, 4 × 3H, *o*-CH*Me*$_2$); 1.20 (d, $^3J_{HH} = 6.8$ Hz, 6H, *p*-CH*Me*$_2$); 1.32 and 1.36 (2s, 2 × 9H, *p*-CMe$_3$ and GeCMe$_3$); 1.72 (s, 18H, *o*-CMe$_3$); 2.79, 2.89 and 3.46 (3 sept, $^3J_{HH} = 6.8$ Hz, 3 × 1H, *o* and *p*-C*H*Me$_2$); 7.07 and 7.13 (2s, 2H, arom H Tip); 7.52 (d, $^4J_{HP} = 0.6$ Hz, arom H Ar).

^{13}C-NMR (C$_6$D$_6$): δ 24.21 (*p*-CH*Me*$_2$); 23.97, 24.51, 25.17 and 25.84 (*o*-CH*Me*$_2$); 30.59 and 31.70 (*p*-C*Me*$_3$ and GeC*Me*$_3$); 34.12 (d, $^1J_{CP} = 4.1$ Hz, Ge*C*Me$_3$); 34.29 (d, $^4J_{CP} = 8.3$ Hz, *o*-C*Me*$_3$); 34.72 (*p*-*C*HMe$_2$); 35.02 (*p*-*C*Me$_3$); 38.63 (*o*-*C*Me$_3$); 40.84 and 41.42 (*o*-*C*HMe$_2$); 121.52 and 121.60 (*m*-CH Tip); 121.95 (*m*-CH Ar), 133.20 (d, $^3J_{CP} = 5.5$ Hz, *ipso*-C Tip); 145.43 (d, $^1J_{CP} = 87.0$ Hz, *ipso*-C Ar); 148.69 and 151.47 (*p*-C Ar and Tip); 152.24 (d, $^2J_{CP} = 2.1$ Hz, *o*-C Ar); 153.26 and 153.64 (*o*-C Tip); 280.82 (d, $^1J_{CP} = 62.1$ Hz, =C=). ^{31}P-NMR (C$_6$D$_6$): δ 249.9.

MS: 622 [M, 6]; 565 [M − *t*-Bu, 3]; 509 [M − 2*t*-Bu + 1, 13]; 465 [M − 2*t*-Bu − *i*-Pr, 2]; 451 [M − 3*t*-Bu, 3]; 379 [M − Ar + 2, 13]; 347 [M − ArP + 1, 3]; 320 [M − Ar − *t*-Bu, 3]; 289 [M − ArP − *t*-Bu, 12]; 275 (ArP − 1, 25); 245 (Ar, 5); 203 (Tip, 4); 57 (*t*-Bu, 100).

3.6. Hydrolysis of **1**

To a solution of **1** prepared from 1.04 g of **7**, in Et$_2$O (10 ml), was added an excess of H$_2$O at r.t. The orange–red color turned immediately yellow. After removal of solvents in vacuo, pentane was added and the reaction mixture dried over Na$_2$SO$_4$. Crystallization at −20 °C from pentane gave 0.73 g of **10** in about 90% purity (75% yield in **10**).

^{1}H-NMR: δ 0.99 and 1.20 (2d, $^3J_{HH} = 6.7$ Hz) and 1.32–1.42 (m, 18H, *o* and *p*-CH*Me*$_2$); 1.27 and 1.31 (2s, 2 × 9H, *p*-CMe$_3$ and GeCMe$_3$); 1.50 (s, 18H, *o*-CMe$_3$); 2.95 (sept, $^3J_{HH} = 6.7$ Hz, 1H, *p*-C*H*Me$_2$); 3.30 (2 sept, $^3J_{HH} = 6.7$ Hz, 2H, *o*-C*H*Me$_2$); 6.99 (s, 2H, arom H Tip); 7.35 (d, $^4J_{HP} = 1.1$ Hz, 2H, arom H Ar); 8.04 (d, $^2J_{HP} = 24.6$ Hz, 1H, P=CH).

^{13}C-NMR: δ 23.91, 24.97, 26.28 and 28.08 (*o* and *p*-CH*Me*$_2$ and GeC*Me*$_3$); 31.42, 31.72, 34.10, 34.17 and 34.53 (*o* and *p*-*C*HMe$_2$ and *o* and *p*-C*Me*$_3$); 29.82 (Ge*C*Me$_3$); 34.96 (*p*-*C*Me$_3$); 38.15 (*o*-*C*Me$_3$); 121.74 and 122.00 (*m*-CH Tip and Ar); 131.11 (d, $^3J_{CP} = 6.0$ Hz *ipso*-C Tip); 144.05 (d, $^1J_{CP} = 69.9$ Hz, *ipso*-C Ar); 149.78 and 149.80 (*p*-C Tip and Ar); 152.66 (*o*-C Ar); 155.15 (*o*-C Tip); 176.90 (d, $^1J_{CP} = 72.2$ Hz, P=CH).

^{31}P-NMR: δ 325.9 (d, $^3J_{PH} = 24.9$ Hz).

MS: 639 [M − 1, 3]; 623 [M − OH, 2]; 583 [M − *t*-Bu, 25]; 565 [M − *t*-Bu − H_2O, 5]; 509 [M − 2*t*-Bu − OH, 32]; 436 [M − Tip-1, 12]; 379 [M − *t*-Bu − Tip − 1, 35]; 351 (*t*-BuGe(Tip)OH, 5); 289 (ArP=CH, 12); 245 (Ar, 5); 233 (ArP=CH − *t*-Bu, 33); 203 (Tip, 10); 57 (*t*-Bu, 100).

3.7. Reaction of **1** with PhCHO, Ph_2CO and R_2CO

The typical procedure is described in the case of fluorenone.

To a solution of **1** in Et_2O (prepared from 1.04 g, 1.54 mmol of **7** and one equivalent of *t*-BuLi) was added a solution of fluorenone (0.28 g, 1.54 mmol) in Et_2O at r.t. The reaction mixture turned yellow. After 1 h stirring, the solvents were evaporated in vacuo and replaced by pentane. Cooling at −20 °C gave light yellow crystals of **13** (m.p. 227 °C, 0.75 g, 61%). **11** and **12** were obtained as viscous oils and could not be completely purified. However, they were obtained in more than 95% purity and were unambiguously identified by their physicochemical data;

11a: ^{1}H-NMR: δ 5.81 (d, $^3J_{HP} = 14.2$ Hz, C*H*Ph), ^{13}C-NMR: δ 90.40 (d, $^2J_{CP} = 20.3$ Hz, *C*HPh), 193.31 (d, $^1J_{CP} = 75.3$ Hz, P=C), ^{31}P-NMR: δ 253.8 (d,$^3J_{PH} =$ 14 Hz).

11b: ^{1}H-NMR: δ 6.10 (d, $^3J_{HP} = 16.8$ Hz, C*H*Ph). ^{13}C-NMR: δ 90.72 (d, $^2J_{CP} = 22.1$ Hz, *C*HPh), 194.60 (d, $^1J_{CP} = 76.4$ Hz, P=C). ^{31}P-NMR: δ 257.7 (d, $^3J_{PH} =$ 17.6 Hz)

MS: 728 [M, 1]; 671 [M − *t*-Bu, 3]; 615 [M − 2*t*-Bu + 1, 3]; 565 [M − *t*-Bu − PhCHO, 2]; 509 [M − 2*t*-Bu-PhCHO + 1, 2]; 435 (ArP=C–CHPh, 5); 377 (ArP=C=CPh, 3); 323 (ArP=CCl, 2); 235 (TipGeO − *i*-Pr + H, 7); 105 (PhCHO − H, 3); 57 (*t*-Bu, 100).

12: ^{1}H-NMR: δ 0.92–1.82 (m, 54 H, *o* and *p*-*t*-Bu, *t*-BuGe, CH*Me*$_2$), 2.95 (sept, $^3J_{HH} = 6.7$ Hz, 2H, *o*-C*H*Me$_2$); (sept, $^3J_{HH} = 6.7$ Hz, 1H, *p*-C*H*Me$_2$); 6.80–8.17 (m, 14H, arom H Tip, Ar and Ph$_2$). ^{13}C-NMR: δ 97.20 (d, $^2J_{CP}$: 29.5 Hz, *C*Ph$_2$), 195.61 (d, $^1J_{CP}$: 71.7 Hz, P=C). ^{31}P-NMR: δ 328.2.

MS: 804 [M, 1]; 747 [M − *t*-Bu, 2]; 691 [M − 2*t*-Bu + 1, 2]; 622 [M − Ph_2CO, 2]; 600 [M − Tip − 1, 2]; 565 [M − Ph_2CO − *t*-Bu, 17]; 559 [M − Ar, 3]; 544 [M − Tip − *t*-Bu, 2]; 509 [M − Ph_2CO − 2*t*-Bu + 1, 13]; 455 (ArP=C=CPh$_2$ + 1, 3); 397 (ArP=C=CPh$_2$ − *t*-Bu, 3); 377 [M − Ph_2CO − Ar, 13]; 350 (TipGe(O)*t*-Bu, 3); 293 (TipGeO, 24); 57 (*t*-Bu, 100).

13: ^{1}H-NMR: δ 0.90 (d, $^3J_{HH} = 6.2$ Hz) and 1.00–1.43 (m, 18H, *o* and *p*-CH*Me*$_2$); 1.10, 1.32, 1.34 and 1.52 (4s, 4 × 9H, *o* and *p*-CMe$_3$); 2.05, 2.95 and 3.15 (3 sept, $^3J_{HH} = 6.7$ Hz, 3 × 1H, *o* and *p*-C*H*Me$_2$); 6.74–7.55 (m, 12H, arom H Tip and Ar, CR$_2$).

^{13}C-NMR: δ 23.97–36.27 (GeC*Me*$_3$, CH*Me*$_2$ and *o* and *p*-C*Me*$_3$); 29.76 (Ge*C*Me$_3$); 34.88 (p-*C*Me$_3$); 38.18 (*o*-*C*Me$_3$); 100.01 (d, $^2J_{CP} = 38.7$ Hz, R*C*O); 132.34 (*ipso*-C Tip); 136.50 (d, $^1J_{CP} = 65.9$ Hz, *ipso*-C Ar); 137.81, 140.30 and 149.26 to 156.14 (*o* and *p*-C Tip and Ar and C of CR$_2$); 193.50 (d, $^1J_{CP} = 60.9$ Hz, P=C). ^{31}P-NMR: δ 314.0.

MS: 802 [M, 1]; 745 [m − *t*-Bu, 1]; 689 [m − 2*t*-Bu + 1, 2]; 622 [M − R_2CO, 1]; 579 [M − R_2CO − *i*-Pr, 1]; 565 [M − R_2CO − *t*-Bu, 16]; 509 [M − R_2CO − 2*t*-Bu, 15]; 453 (ArP=CCR$_2$ + 1, 2); 275 (ArP − 1, 23); 203 (Tip, 2); 57 (*t*-Bu, 100).

3.8. X-ray measurements of **13**

Suitable crystals were obtained by crystallization from $CHCl_3$ at r.t. Crystal data for **13** are presented in Table 2. All data were collected at low temperatures on a Bruker-AXS CCD 1000 diffractometer with Mo–K$_\alpha$ radiation ($\lambda = 0.71073$ Å). The structure was solved by direct methods by means of SHELXL-97 [24] and refined with all data on F^2 by means of SHELXS-97 [25]. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms of the molecules were geometrically idealized and refined using a riding model. Disorders of a *t*-Bu- and a *i*-Pr-group has been refined with the help of ADP and distances restraints.

4. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 166267 for compound **13**. Copies of this information may be obtained free of charge from The Director, CCDC, 12, Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.camc.ac.uk or www: http://www.ccdc.camc.ac.uk).

Acknowledgements

Y.E.H. thanks the ‘Comité Mixte Inter-universitaire Franco-Marocain’ (Action Intégrée no 216 SM 00). The authors thank INTAS (project no 97 30344) and the CNRS for financial support.

References

[1] R. Appel, in: M. Regitz, O.J. Scherer (Eds.), Multiple Bonds and Low Coordination in Phosphorus Chemistry, Thieme, Stuttgart, 1990, p. 157.

[2] J. Escudié, H. Ranaivonjatovo, L. Rigon, Chem. Rev. 100 (2000) 3639.

[3] B. Eichler, R. West, Adv. Organomet. Chem. 46 (2001) 1.

[4] (a) G. Miracle, J.L. Ball, D.R. Powell, R. West, J. Am. Chem. Soc. 115 (1993) 11598;

(b) G.E. Miracle, J.L. Ball, S.R. Bielmeier, D.R. Powell, R. West, in: B. Marciniec, J. Chojnowski (Eds.), Progress in Organosilicon Chemistry, Gordon and Breach Science Publishers, Basel, 1995, p. 83;
(c) M. Trommer, G.E. Miracle, B.E. Eichler, D.R. Powell, R. West, Organometallics 16 (1997) 5737;
(d) B.E. Eichler, G.E. Miracle, D.R. Powell, R. West, Main Group Met. Chem. 22 (1999) 147.

[5] (a) K. Kishikawa, N. Tokitoh, R. Okazaki, Organometallics 16 (1997) 5127;
(b) N. Tokitoh, K. Kishikawa, R. Okazaki, Chem. Lett. (1998) 811;
(c) B.E. Eichler, D.R. Powell, R. West, Organometallics 17 (1998) 2147;
(d) B.E. Eichler, D.R. Powell, R. West, Organometallics 18 (1999) 540.

[6] (a) C. Kerst, C.R. Ruffolo, W.J. Leigh, Organometallics 16 (1997) 5804;
(b) C. Kerst, C.W. Rogers, C.R. Ruffolo, W.J. Leigh, J. Am. Chem. Soc. 119 (1997) 466.

[7] (a) G. Maier, H.P. Reisenauer, H. Egenolf, Organometallics 18 (1999) 2155;
(b) M.A. Pearsall, R. West, J. Am. Chem. Soc. 110 (1998) 7228;
(c) C.A. Arrington, J.T. Petty, S.E. Payne, W.C.K. Haskins, J. Am. Chem. Soc. 110 (1998) 6240;
(d) M. Tacke, C. Klein, D.J. Stufkens, A. Oskam, P. Jutzi, E.A. Bunte, Z. Anorg. Allg. Chem. 619 (1993) 865.

[8] (a) M. Weidenbruch, B. Brand-Roth, S. Pohl, W. Saak, Angew. Chem. Int. Ed. Engl. 29 (1990) 90;
(b) M. Weidenbruch, B. Brand-Roth, S. Pohl, W. Saak, Polyhedron 10 (1991) 1147;
(c) N. Takeda, H. Suzuki, N. Tokitoh, R. Okazaki, S. Nagase, J. Am. Chem. Soc. 119 (1997) 1456.

[9] H. Grützmacher, S. Freitag, R. Herbst-Irmer, G.S. Sheldrick, Angew. Chem. Int. Ed. Engl. 31 (1992) 437.

[10] L. Rigon, H. Ranaivonjatovo, J. Escudié, A. Dubourg, J.-P. Declercq, Chem. Eur. J. 5 (1999) 774.

[11] H. Ramdane, H. Ranaivonjatovo, J. Escudié, S. Mathieu, N. Knouzi, Organometallics 15 (1996) 3070.

[12] S.J. Goede, F. Bickelhaupt, Chem. Ber. 124 (1991) 2677.

[13] (a) M. Van der Sluis, J.B.M. Wit, F. Bickelhaupt, Organometallics 15 (1996) 174;
(b) M. Yoshifuji, H. Kawanami, Y. Kawai, K. Toyota, M. Yasunami, T. Niitsu, N. Inamoto, Chem. Lett. (1992) 1053;
(c) E. Niecke, M. Nieger, O. Schmidt, D. Gudat, W.W. Schoeller, J. Am. Chem. Soc. 121 (1999) 519.

[14] H. Ranaivonjatovo, H. Ramdane, H. Gornitzka, J. Escudié, J. Satgé, Organometallics 17 (1998) 1631.

[15] M. Lazraq, C. Couret, J. Escudié, J. Satgé, M. Dräger, Organometallics 10 (1991) 1771.

[16] (a) A.G. Brook, W.J. Chatterton, J.F. Sawyer, D.W. Hughes, K. Vorspohl, Organometallics 6 (1987) 1246;
(b) A.G. Brook, K. Vorspohl, R.R. Ford, M. Hesse, W.J. Chatterton, Organometallics 6 (1987) 2128.

[17] S. Masamune, S.A. Batcheller, J. Park, W.M. Davis, O. Yamashita, Y. Ohta, Y. Kabe, J. Am. Chem. Soc. 111 (1989) 1888.

[18] M. Lazraq, C. Couret, J.P. Declercq, A. Dubourg, J. Escudié, M. Rivière-Baudet, Organometallics 9 (1990) 845.

[19] L. Ross, M. Dräger, Z. Naturforsch. 39B (1984) 868.

[20] K.M. Baines, W.G. Stibbs, Coord. Chem. Rev. 145 (1995) 157.

[21] T. Matsumoto, N. Tokitoh, R. Okazaki, Chem. Commun. (1997) 1553.

[22] M. Dräger, L. Ross, D. Simon, Rev. Silicon Germanium, Tin, Lead Compound 7 (1983) 299.

[23] M. Andrianarison, C. Couret, J.-P. Declercq, A. Dubourg, J. Escudié, J. Satgé, J. Chem. Soc. Chem. Commun. (1987) 921.

[24] G.M. Sheldrick, Acta Crystallogr. Sect. A 46 (1990) 467.

[25] G.M. Sheldrick, SHELXL-97, Program for Crystal Structure Refinement, Universität Göttingen, Germany, 1997.