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From a Transient 3-Germa-1-phosphabutadiene to a 1,2-Bis(phosphaalkenyl)-1,2-digermacyclobutane

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Dehydrofluorination of the fluoro(fluorenyl)(phosphaalkenyl)germane **7** by *tert*-butyllithium in the presence of chlorotrimethylsilane affords the 1,2-bis(phosphaalkenyl)-1,2-digermacyclobutane **2**. This reaction probably involves the prior formation of the transient 3-germa-1-phosphabutadiene **1**, followed by its head-to-head dimerization. **2** contains a distorted four-membered ring with long intracyclic Ge−Ge (2.5567(8) Å), Ge−C(R_2) (2.058(4) Å), and (R_2)C−C(R_2) (1.592(6) Å) bonds; mesityl groups are trans in relation to this heterocycle.

Introduction

Double-bonded compounds of germanium are now well-known:[1] thus, heavy homologues of many important organic functions such as alkenes, imines, ketones, thioketones, etc. have been synthesized and stabilized, generally owing to a large steric hindrance allowing their isolation as monomers. In contrast, heavy homologues of dienes or heterodienes with a doubly bonded germanium of type A ($X{=}C(R)C(R'){=}Ge{<}$) or B ($X{=}C(R)Ge(R'){=}C{<}$) are still unknown. Such derivatives should be interesting to study in order to determine if they behave as germenes or as germadienes and, thus, if the $Ge{=}C$ and $C{=}X$ double bonds react as two isolated systems or if there is a conjugation between these two double bonds. In this matter, B should be particularly interesting since theoretical calculations on the 2,3-digermabutadiene $H_2C{=}GeHGeH{=}CH_2$ predicted that the conjugation through germanium atoms was higher than expected and about half of that observed in 1,3-butadiene.[2] Thus, conjugation between the two double bonds should exist in derivatives B, and a "diene" behavior could be expected.

In this paper, we present the attempted synthesis of a compound of type B, in which X is a phosphorus atom, the 3-germa-1-phosphabutadiene $ArP{=}C(Cl)Ge(Mes){=}CR_2$ (**1**).

Results and Discussion

Attempted Synthesis of 1. We chose as the substituent on phosphorus the very bulky 2,4,6-tri-*tert*-butylphenyl group (Ar), which has served well in the stabilization of dicoordinate P species[3] and included the carbon 4 in the fluorenylidene group which also is known to stabilize germenes $R'R''Ge{=}CR_2$.[4] Due to the usual high reactivity of the $Ge{=}C$ double bond, the $P{=}C$ moiety was created first since, when phosphorus is substituted by the very bulky Ar group, the $P{=}C$ double bond is generally almost inert. For the coupling of the $P{=}C$ moiety with the $GeCHR_2$ moiety we used the carbenoid $ArP{=}C(Cl)Li$ (**4**),[5] which is much more stable than its bromo analogue.[6]

Treatment of carbenoid **4**, obtained by reaction of dichlorophosphaalkene **3** with *n*-butyllithium, with difluoro(mesityl)(fluorenyl)germane **5**[7] afforded the fluoro(phosphaalkenyl)germane **7** in good yield. In contrast, the chloro analogue **8** was obtained only in very low yield (~10%). However, the chloro(phosphaalkenyl)germane **8** could be prepared in satisfactory yield by a two-step procedure involving the prior reaction of **4** with trichloromesitylgermane (**9**) (leading to **10**), followed by the addition of fluorenyllithium (Scheme 1).

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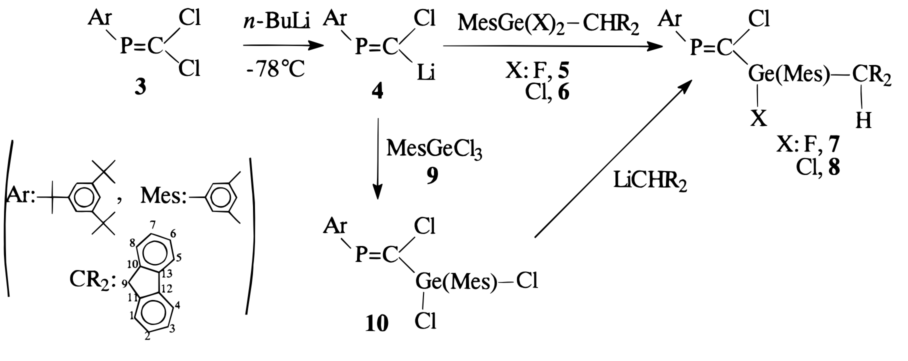
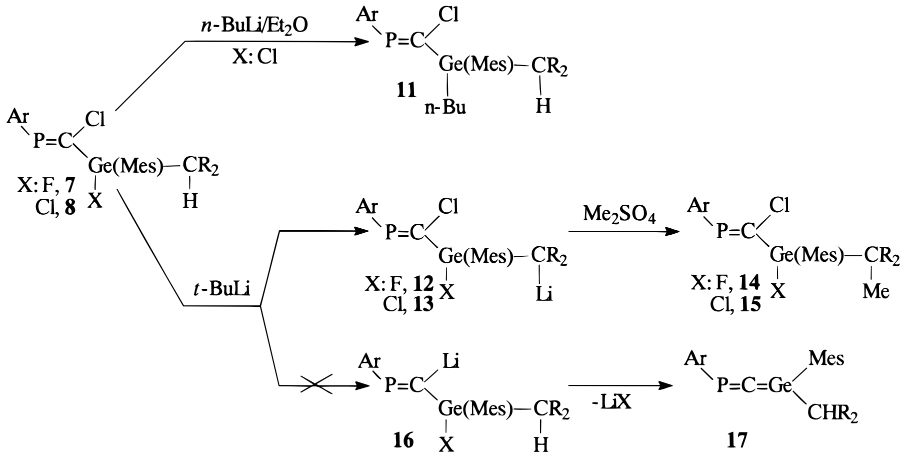
Scheme 1



Scheme 2



Only one isomer of **7** or **8** was formed, probably the *E* isomer. The formation of *E* isomers can be reasonably explained by the preferential substitution of chlorine at the less hindered side of the P=C double bond to form the *Z* carbenoid.[6] This configuration was confirmed by the X-ray structure of the compound derived from the reaction between **7** and *tert*-butyllithium (see X-ray Structure of **2**).

Attempts to dehydrochlorinate **8** with *n*-butyllithium failed; only the alkylation of germanium was observed, leading to **11**. In contrast, with the bulkier and more basic *tert*-butyllithium, the expected lithium compounds **12** and **13** were formed immediately at low temperature. Quenching with dimethyl sulfate afforded respectively **14** and **15**. The Li/Cl exchange on sp^2-hybridized carbon to lead to **16**, precursor of the germaphosphaallene **17**, did not occur, the formation of **12** and **13** being much more rapid (Scheme 2).[8]

The lithium compounds **12** and **13** are quite stable, since they were recovered unchanged after some hours at room temperature and **13** ($X = Cl$) even survived in refluxing Et_2O. Heating **12** ($X = F$) at 35 °C for 1 h led to its partial decomposition with the formation of dimeric **2** but only in low yield (~10%) mixed with unidentified products (Scheme 3).

The complete and nearly quantitative delithiofluorination of **12** leading to **2** occurred when 1 equiv of chlorotrimethylsilane was added. In contrast, addition of chlorotrimethylsilane to **13** yielded the stable and isolable silylfluorenyl derivative **18**. The formation of **2** from **12** can be rationalized in terms of fluorine/chlorine exchange at germanium, with the formation of the (chlorogermyl)lithium compound **13**. Such a reaction, with further elimination of chlorotrimethylsilane, has already been reported by Klingebiel in the synthesis of (t-Bu)$_2$Si=NAr (Ar = 2,4,6-tri-*tert*-butylphenyl).[9] However, as **13** is stable under the experimental conditions when directly formed from **8** and *tert*-butyllithium, such a route seems to be ruled out. The transient formation of **19** with a rapid elimination of fluorotrimethylsilane (route a) also is a possibility. A similar elimination of Me_3SiF from Cp*Ge(X)(F)CR_2SiMe_3 has previously been reported[10] but occurred only after heating at 140 °C (or at 100 °C in the presence of Et_3N), which is not the case here. In our experiment, a large lengthening of the CR_2−Si and Ge−F bonds due to the high steric hindrance could explain the very easy elimination of Me_3SiF. However, the steric congestion in **1** is not too great, since it can dimerize. Thus, for all these reasons, an electrophilic assistance of chlorotrimethylsilane with a concerted or nearly concerted six-center mechanism (route b) seems the most likely. Such a mechanism was postulated by Wiberg and Wagner for the formation of silene Me_2Si=C($SiMe_3$)SiMe(t-Bu)$_2$[11] (Scheme 3).

Characterization of 1,2-Bis(phosphaalkenyl)-1,2-digermacyclobutane 2. **2** was isolated in the form of

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[8] The first allenic derivative of germanium, the germaphosphaallene Mes_2Ge=C=PAr, has been prepared by a similar reaction from Mes_2Ge(F)C(Br)=PAr and *n*-butyllithium, via Mes_2Ge(F)C(Li)=PAr by a Br/Li exchange on the sp^2 carbon: Ramdane, H.; Ranaivonjatovo, H.; Escudié, J.; Mathieu, S.; Knouzi, N. *Organometallics* **1996**, *15*, 3070.

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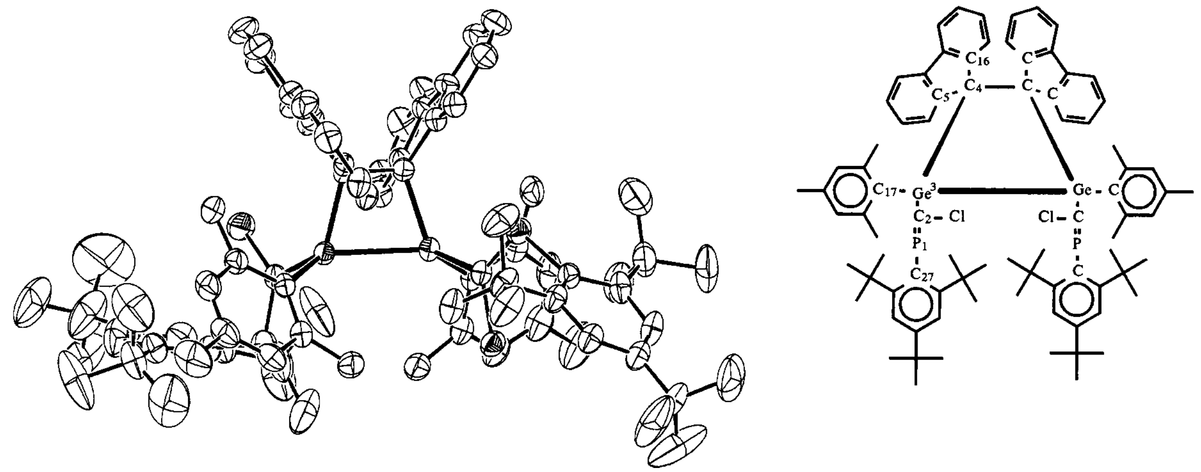
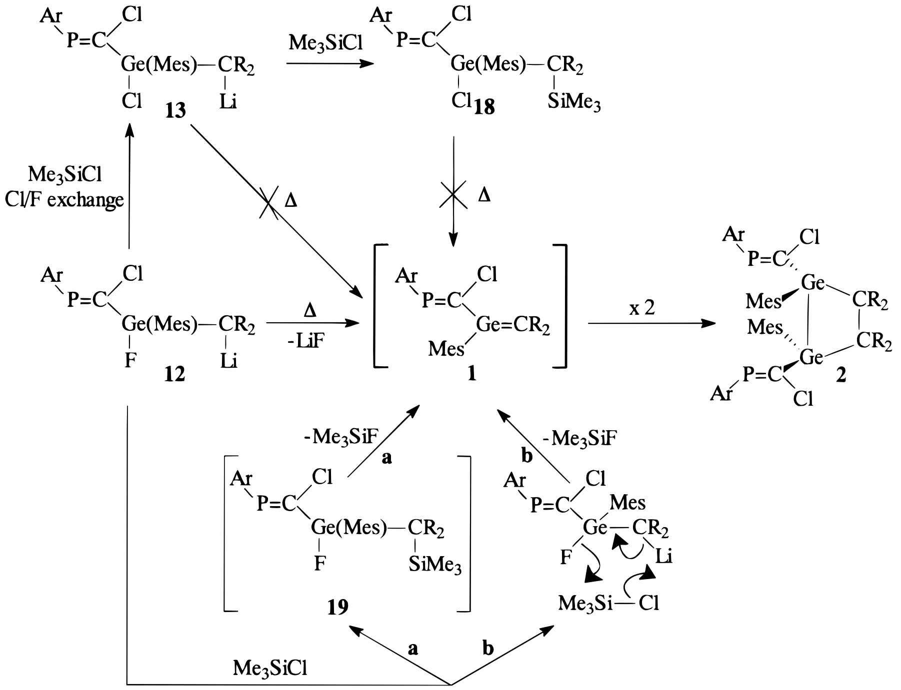


Figure 1. PLATON view of **2**. Ellipsoids are drawn at the 30% probability level.

Scheme 3



air-stable yellow crystals after crystallization from pentane. NMR spectra and the X-ray study proved that **2** was the head-to-head dimer of the expected 3-germa-1-phosphabutadiene **1**. A striking feature in the ^{1}H NMR spectrum was the large difference of chemical shift (2.18 ppm) between the two *o*-methyl groups of the mesityl, respectively at 0.87 and 3.05 ppm. Such a $\Delta\delta$ value proves the hindered rotation of the mesityl group at 30 °C and the very different positions of these two methyls in relation to the highly anisotropic fluorenylidene group. The X-ray structure of **2** confirms this assessment, showing that one methyl is close to the center of one aromatic group of the fluorenylidene, the other one being rather far away. In the ^{13}C NMR spectrum, a doublet was observed at an unusually low field for the carbon atom of the fluorenylidene group which is bonded to the germanium atom (72.34 ppm, $^3J_{CP} = 4.5$ Hz). Such a doublet shows coupling with only one phosphorus atom and proves the formation of the head-to-head dimer **2** versus the head-to-tail dimer, in which a triplet should be observed. Mass spectrometry gives additional proof of the head-to-head structure, since one of the main fragments (*m*/*z* 328) is the difluorenylidene $R_2C{=}CR_2$.

X-ray Structure of 2. Figure 1 gives a PLATON view and Figure 2 a stereoscopic view of **2**; crystal data and structure refinement details are given in Table 1, bond lengths and bond angles in Table 2, and torsion angles in Table 3.

As two independent molecules are present in the unit cell, four $ArP{=}C(Cl)Ge(Mes)CR_2$ moieties exist. Since there are only slight differences in bond lengths, bond angles, and torsion angles between them, we give generally only average values for each of these data. The molecule possesses an approximate C_2 axis which bisects both the $(R_2)C{-}C(R_2)$ and Ge−Ge bonds of the four-membered ring. The only lack of symmetry is observed for the P=C−Cl moiety, since within the same molecule, rather important differences are observed for the P(1)−C(2)−Ge(3) and Cl−C(2)−Ge(3) bond angles; e.g., they are respectively 125.8(2) and 118.1(2)° for P(1A)−C(2A)−Ge(3A) and P(1B)−C(2B)−Ge(3B) and

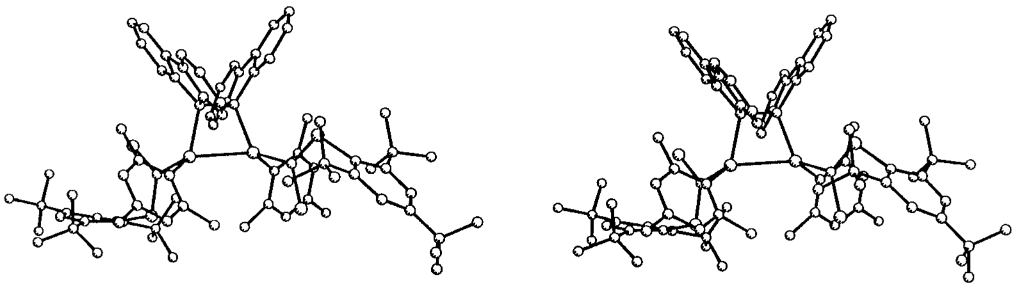


Figure 2. Stereoscopic view of **2**.

Table 1. Crystal Data and Structure Refinement for 2

empirical formula	$C_{82}H_{96}Cl_2Ge_2P_2$
fw	1359.61
temp	293(2) K
wavelength	0.710 69 Å
cryst syst, space group	triclinic, $P\bar{1}$
unit cell dimensions	$a = 12.979(2)$ Å $b = 16.464(3)$ Å $c = 36.596(5)$ Å $\alpha = 87.92(1)°$ $\beta = 89.19(1)°$ $\gamma = 86.89(1)°$
V	7803(2) Å^3
Z, calcd density	4, 1.157 Mg/m^3
abs coeff	0.920 mm^{-1}
$F(000)$	2864
cryst size	0.32 × 0.28 × 0.25 mm
θ range for data collecn	2.91−24.41°
limiting indices	$0 \le h \le 15$, $-19 \le k \le 19$, $-41 \le l \le 42$
no. of rflns collected/unique	60 716/23 772 (R(int) = 0.045)
completeness to θ = 24.41°	92.6%
refinement method	full-matrix least squares on F^2
no. of data/restraints/params	23772/764/1585
goodness of fit on F^2	1.022
final R indices ($I > 2\sigma(I)$)	R1 = 0.0496, wR2 = 0.1317
R indices (all data)	R1 = 0.0945, wR2 = 0.1501
largest diff peak and hole	0.538 and −0.368 e Å^{-3}

Table 2. Bond Lengths (Å) and Angles (deg) for 2 (with Their Esd's in Parentheses)

	Bond Lengths		
P(1)−C(2)	1.664(4)	Ge(3)−C(4)	2.058(4)
P(1)−C(27)	1.851(4)	Ge−Ge	2.5567(8)
C(2)−Cl	1.744(4)	C(4)−C(16)	1.520(5)
C(2)−Ge(3)	2.002(4)	C(4)−C(5)	1.528(5)
Ge(3)−C(17)	1.978(4)	(R_2)C−C(R_2)	1.592(6)
	Bond Angles		
C(2)−P(1)-C(27)	105.4(2)	P(1)−C(2)−Cl	122.9(2)
P(1A)−C(2A)−Ge(3A)	125.8(2)	P(1B)−C(2B)−Ge(3B)	118.1(2)
P(1C)−C(2C)−Ge(3C)	118.2(2)	P(1D)−C(2D)−Ge(3D)	126.7(2)
Cl(A)−C(2A)−Ge(3A)	111.1(2)	Cl(B)−C(2B)−Ge(3B)	117.6(2)
Cl(C)−C(2C)−Ge(2C)	118.4(2)	Cl(D)−C(2D)−Ge(2D)	110.3(2)
C(17)−Ge(3)−C(2)	99.36(16)	C(16)−C(4)−C(5)	101.6(3)
C(17)−Ge(3)−C(4)	114.79(16)	C(16)−C(R_2)−C(R_2)	112.6(3)
C(2)−Ge(3)−C(4)	120.62(16)	C(5)−C(R_2)−C(R_2)	112.7(3)
C(17)−Ge−Ge	125.17(12)	C(16)−C(4)−Ge(3)	103.6(3)
C(2)−Ge−Ge	121.48(13)	C(5)−C(4)−Ge(3)	124.4(3)
C(4)−Ge−Ge	75.33(11)	C(R_2)−C(R_2)−Ge(3)	101.8(2)

111.2(2) and 117.6(2)° for Cl(A)−C(2A)−Ge(3A) and Cl(B)−C(2B)−Ge(3B). This also is observed in all the torsion angles around the C(2)−Ge(3) bond; e.g., P(1A)−C(2A)−Ge(3A)−C(17A) = 111.5(3)° and P(1B)−C(2B)−Ge(3B)−C(17B) = −57.9(3)°. The second independent molecule displays the same differences.

Table 3. Torsion Angles (deg) for 2 (with Their Esd's in Parentheses)[a]

C(27)−P(1)−C(2)−Cl	0.5(4)
C(27)−P(1)−C(2)−Ge(3)	170.6(3)
C(2)−Ge(3)−Ge(3)−C(2)	139.7(11)
C(17)−Ge(3)−Ge(3)−C(17)	125.5(2)
C(4)−Ge(3)−Ge(3)−C(4)	14.11(16)
Ge(3)−Ge(3)−C(4)−C(4)	18.13(11)
Ge(3)−C(4)−C(4)−Ge(3)	22.5(2)
Ge(3)−Ge(3)−C(4)−C(4)	18.2(2)

[a] Average values are given; thus, the sign has been omitted.

The trapezoidal digermacyclobutane ring deviates from planarity with folding angles of, respectively, 26.4 and 24.8° along the Ge(3)−C(4) axes in the two independent molecules. The two mesityl groups as well as the ArP=C(Cl) groups are trans in relation to the four-membered ring. Long distances are observed for the intracyclic Ge−Ge, Ge−C(R_2), and (R_2)C−C(R_2) bonds: 2.5567(8) Å for Ge−Ge, at the upper limit of the range which is 2.40−2.50 Å,[12] 2.058(4) Å for Ge−C(R_2) (∼1.95−1.99 Å for the classical Ge−C bond length),[12] and 1.592 Å for the (R_2)C−C(R_2) bond length instead of 1.54 Å. The increase in the bond lengths is due to the large steric hindrance. A lesser lengthening of the Ge−C(2) bond (2.002(4) Å) is also observed, whereas the Ge−C(17) length (1.978(4) Å) lies almost in the normal range. The arrangement around the P=C double bond is nearly planar (C(27)P(1)C(2)Cl, −0.3(3)°; sum of angles on C(2), 359.5°) with an *E* configuration. Normal values are observed for C(27)−P(1), P(1)=C(2), and C(2)−Cl bond lengths.

A 1,2-digermacyclobutane has been obtained by Apeloig and co-workers[13] by a head-to-head dimerization of adamantylidenegermene $(Me_3Si)_2Ge$=Ad (Ad = 2-adamantylidene).

This molecule has longer Ge−C and C−C bonds than **2** (respectively 2.097(7) and 1.63(1) Å) but a much shorter Ge−Ge bond (2.422(2) Å). Other 1,2-digermacyclobutanes[14,15] and 1,4-digermabicyclo[2.2.0]hexanes[15,16] (thus, including two 1,2-digermacyclobutane rings) have been prepared from germylenes and alkenes. Such heterocycles also display long intracyclic Ge−Ge, Ge−C, and C−C bonds; however, these are not as long as those bonds in **2**.

The isolation of the head-to-head dimer **2** proves the intermediate formation of the transient 3-germa-1-

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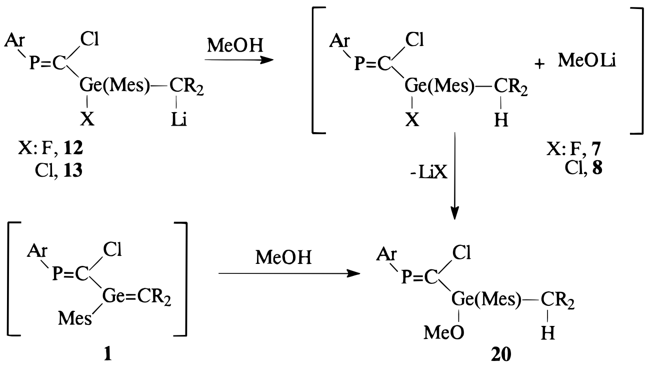
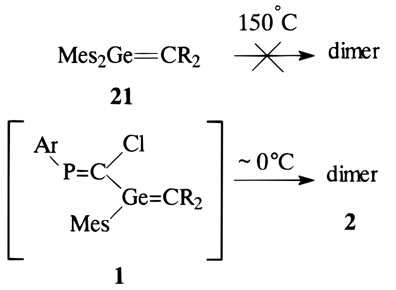
Scheme 4



Scheme 5



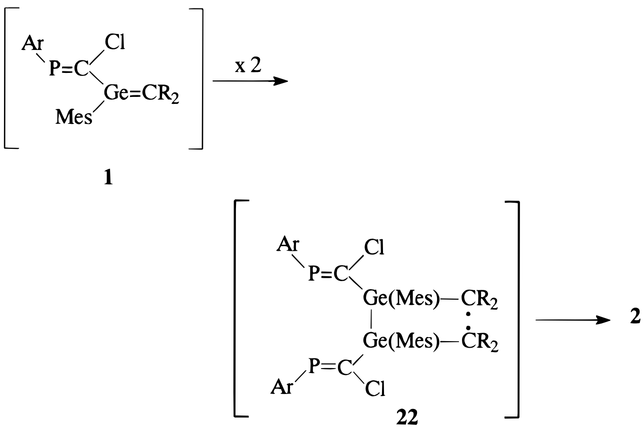
phosphabutadiene **1**. Even though this intermediate has not been obtained, the lithium compounds **12** and **13** can be considered, to some extent, as synthetic equivalents of **1**, since addition of methanol affords quantitatively the methoxygermane **20** (Scheme 4).

The facile dimerization of 3-germa-1-phosphabutadiene **1** is surprising since the germene $Mes_2Ge{=}CR_2$ (**21**), with the same group on carbon and two mesityl substituents on germanium instead of one mesityl and a $ArP{=}C(Cl)$ group, is very thermally stable and resistant to dimerization.[4a] It is recovered unchanged after heating at 150 °C for a few hours (Scheme 5). The behavior of **1** could be due to the lesser steric hindrance of $ArP{=}C(Cl)$ group (vs that of the mesityl group) as well as the less polarized $Ge{=}C$ double bond in this molecule.

In the absence of a trapping reagent, the most common pathway of transient germenes is head-to-tail dimerization, which is consistent with the polarization $Ge^{\delta+}{=}C^{\delta-}$.[1] The head-to-head dimerization is a less common mode of dimerization.[1] The same behavior was observed for some silenes $>Si{=}C<$,[17,18] but until now only head-to-tail dimerization has been observed for stannenes $>Sn{=}C<$.[19]

The mechanisms by which silenes dimerize have been the subject of intense interest and controversy for theoreticians.[20] According to most of the papers, 1,2-disilacyclobutanes are formed from silenes by a process believed to be initiated by silicon−silicon bond formation. Thus, in our case, we can postulate the preliminary formation of a Ge−Ge bond involving the 1,4-diradical species **22**, whose radical centers are located on carbon. This diradical then couples to give dimer **2** (Scheme 6).[21] The dimerization is stereoselective, since only the dimer is formed in which the same groups on germanium are trans in relation to the four-membered ring. This could be due to the large difference of steric hindrance between Mes and $ArP{=}C(Cl)$. However, other mechanisms cannot be excluded.

Scheme 6



Our efforts are now directed toward substitution on phosphorus and germanium by bulkier groups in order to stabilize such germaphosphabutadienes against dimerization.

Experimental Section

General Experimental Considerations. All experiments were carried out in flame-dried glassware under an atmosphere of nitrogen. 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) and Bruker AC 250 (62.89 MHz) (reference TMS); ^{19}F, Bruker AC 80 (75.39 MHz) (reference CF_3COOH); ^{31}P, Bruker AC 200 (80.01 MHz) (reference 85% H_3PO_4). The NMR solvent was always $CDCl_3$. Melting points were determined on a Leitz 350 apparatus. Mass spectra were collected on a Hewlett-Packard 5989 A spectrometer by EI at 70 eV referenced to ^{74}Ge. Elemental analyses were performed by the "Service de Microanalyse de l'Ecole de Chimie de Toulouse".

$ArP{=}CCl_2$ was prepared according to the procedure of Bickelhaupt from $ArPCl_2$, $CHCl_3$, and *n*-BuLi at low temperature (−90 °C).[6a]

Synthesis of $ArP{=}C(Cl)Ge(Mes)(F)CHR_2$ (7). $ArP{=}C(Li)Cl$ (**4**) was prepared by adding *n*-BuLi (1.80 mL, 1.6 M in hexane) to $ArP{=}CCl_2$ (**3**; 1.00 g, 2.78 mmol) in THF (15 mL), cooled to −78 °C. To this brown reaction mixture was added a solution of $MesGe(F)_2CHR_2$ (**5**; 1.09 g, 2.78 mmol) in THF (15 mL) cooled to −78 °C. After 30 min of stirring at this temperature, the brown reaction mixture was gradually warmed to room temperature. After removal of THF in vacuo, pentane (40 mL) was added and LiF was removed by filtration. Recrystallization from pentane afforded 1.50 g (77%) of **7** as a light yellow powder (mp 177 °C).

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[21] In the dimerization of silenes involving the preliminary formation of a Si−Si bond, various types of dimers (head-to-head, disilanaphthalene, or linear) are obtained, depending on the substituents on the silene carbon.[18]

^{1}H NMR: δ 1.32 (s, 9H, *p*-*t*-Bu), 1.39 (s, 18H, *o*-*t*-Bu), 2.05 (d, $^{5}J_{HF}$ = 2.3 Hz, 6H, *o*-Me of Mes), 2.17 (s, 3H, *p*-Me of Mes), 4.88 (broad s, 1H, C*H*R$_2$), 6.66 (s, 2H, arom H of Mes), 7.18−7.85 (m, 8H, CR$_2$), 7.39 (d, $^{4}J_{HP}$ = 1.5 Hz, 2H, arom H of Ar). ^{13}C NMR: δ 21.2 (*p*-Me of Mes), 23.6 (d, $^{4}J_{CF}$ = 5.1 Hz, *o*-Me of Mes), 31.4 (*p*-C*Me$_3$*), 32.9 (d, $^{4}J_{CP}$ = 6.6 Hz, *o*-C*Me$_3$*), 35.1 (*p*-*C*Me$_3$), 37.8 and 37.9 (*o*-*C*Me$_3$), 44.7 (dd, $^{2}J_{CF}$ = 11.9 Hz, $^{3}J_{CP}$ = 5.1 Hz, *C*HR$_2$), 120.1 and 120.2 (C$_4$C$_5$), 122.1 and 122.2 (*m*-C of Ar), 124.8, 125.7 and 126.6 (C$_1$C$_2$C$_3$C$_6$C$_7$C$_8$), 128.3 (*ipso*-C of Mes), 129.0 (*m*-C of Mes), 134.0 (d, $^{1}J_{CP}$ = 64.9 Hz, *ipso*-C of Ar), 140.3, 140.9, 141.4, 142.3, 142.4 and 142.5 (*p*-C of Mes, C$_{10}$C$_{11}$C$_{12}$C$_{13}$), 143.7 (*o*-C of Mes), 151.0 (*p*-C of Ar), 153.5 (*o*-C of Ar), 165.6 (dd, $^{1}J_{CP}$ = 87.7 Hz, $^{2}J_{CF}$ = 9.0 Hz, P=C). ^{19}F NMR: δ −100.1 (d, $^{3}J_{FP}$ = 26.8 Hz).^{31}P NMR: δ 305.1 (d, $^{3}J_{PF}$ = 26.8 Hz). MS (*m*/*z*): 700 (M, 10), 665 (M − Cl, 7), 535 (M − CHR$_2$, 40), 499 (M − CHR$_2$ − Cl − 1, 20), 287 (ArP=C − 1, 45), 165 (CHR$_2$, 82), 57 (*t*-Bu, 100). Anal. Calcd for C$_{41}$H$_{49}$ClFGeP: C, 70.36; H, 7.06. Found: C, 70.41; H, 7.22.

Synthesis of ArP=C(Cl)Ge(Cl$_2$)Mes (10). To a solution of ArP=CCl$_2$ (**3**; 1.20 g, 3.35 mmol) in THF (15 mL) cooled to −78 °C was added *n*-BuLi (2.30 mL, 1.6 M in hexane, 3.68 mmol). After 45 min of stirring at this temperature, a solution of ArP=C(Li)Cl (**4)** was slowly added to a solution of MesGeCl$_3$ (1.00 g, 3.35 mmol) in THF (15 mL) cooled to −78 °C. The reaction mixture turned black-brown. It was stirred for 30 min at this temperature and then gradually warmed to 20 °C. After removal of solvents in vacuo, pentane (30 mL) was added and LiCl was filtered off. Elimination of pentane in vacuo afforded 1.56 g (80%) of **10** (mp 165 °C) as a light brown oil which slowly solidified.

^{1}H NMR: δ 1.38 (s, 9H, *p*-*t*-Bu), 1.52 (s, 18H, *o*-*t*-Bu), 2.33 (s, 3H, *p*-Me of Mes), 2.68 (s, 6H, *o*-Me of Mes), 6.95 (s, 2H, arom H of Mes), 7.48 (d, $^{4}J_{HP}$ = 1.6 Hz, 2H, arom H of Ar). ^{13}C NMR: δ 22.5 (*p*-Me of Mes), 25.9 (*o*-Me of Mes), 31.7 (*p*-C*Me$_3$*), 33.0 (d, $^{4}J_{CP}$ = 6.8 Hz, *o*-C*Me$_3$*), 35.2 (*p*-*C*Me$_3$), 38.0 (*o*-*C*Me$_3$), 122.5 (*m*-C of Ar), 130.2 (*m*-C of Mes), 132.7 (d, $^{1}J_{CP}$ = 63.3 Hz, *ipso*-C of Ar), 142.0 (*p*-C of Mes), 143.5 (*o*-C of Mes), 151.5 (*p*-C of Ar), 153.8 (d, $^{2}J_{CP}$ = 3.0 Hz, *o*-C of Ar), 164.5 (d, $^{1}J_{CP}$ = 91.2 Hz, P=C). ^{31}P NMR: δ 301.9. MS (*m*/*z*): 586 (M, 16), 571 (M − Me, 92), 537 (M − Me − Cl + 1, 17), 529 (M − *t*-Bu, 14), 323 (ArP=CCl, 16), 275 (ArP − 1, 38), 119 (Mes, 21), 57 (*t*-Bu, 100). Anal. Calcd for C$_{28}$H$_{40}$Cl$_3$GeP: C, 57.34; H, 6.87. Found: C, 57.50; H, 6.95.

Synthesis of ArP=C(Cl)Ge(Mes)(Cl)CHR$_2$ (8). To a solution of **10** (1.95 g, 3.33 mmol) in Et$_2$O (15 mL) cooled to 0 °C was added 1 equiv of R$_2$CHLi (prepared from fluorene (0.55 g, 3.31 mmol) and *n*-BuLi (2.20 mL, 1.6 M in hexane, 3.52 mmol)). After the end of the addition, the brown reaction mixture was warmed to room temperature and stirred for 30 min. The solvents were removed in vacuo, 30 mL of pentane was added, and LiCl was removed by filtration. Crystallization from pentane afforded 2.02 g (85%) of **8** as a yellow powder (mp 188 °C).

^{1}H NMR: δ 1.30 (s, 27H, *t*-Bu), 2.24 (s, 3H, *p*-Me of Mes), 2.30 (s, 6H, *o*-Me of Mes), 4.90 (broad s, 1H, C*H*R$_2$), 6.77 (broad s, 2H, arom H of Mes), 7.10−7.90 (m, 8H, CR$_2$), 7.33 (d, $^{4}J_{HP}$ = 1.6 Hz, 2H, arom H of Ar). ^{13}C NMR: δ 21.1 (*p*-Me of Mes), 24.8 (*o*-Me of Mes), 31.4 (*p*-C*Me$_3$*), 33.0 (d, $^{4}J_{CP}$ = 7.0 Hz, *o*-C*Me$_3$*), 35.0 (*p*-*C*Me$_3$), 37.8 (*o*-*C*Me$_3$), 46.3 (d, $^{3}J_{CP}$ = 5.1 Hz, *C*HR$_2$), 120.0 and 120.1 (C$_4$C$_5$), 122.0 and 122.2 (*m*-C of Ar), 124.8−126.8 (C$_1$C$_2$C$_3$C$_6$C$_7$C$_8$), 128.5 (*ipso*-C of Mes), 129.8 (*m*-C of Mes), 133.9 (d, $^{1}J_{CP}$ = 57.0 Hz, *ipso*-C of Ar), 140.3, 141.6, 141.9, 142.4, and 142.8 (*p*-C of Mes, C$_{10}$C$_{11}$C$_{12}$C$_{13}$), 143.8 (*o*-C of Mes), 150.8 (*p*-C of Ar), 153.3 and 153.8 (*o*-C of Ar), 164.8 (d, $^{1}J_{CP}$ = 91.7 Hz, P=C). ^{31}P NMR: δ 299.7. MS (*m*/*z*): 716 (M, 3), 681 (M − Cl, 12), 551 (M − CHR$_2$, 78), 515 (M − CHR$_2$ − Cl − 1, 35), 495 (M − CHR$_2$ − *t*-Bu + 1, 26), 459 (M − CHR$_2$ − *t*-Bu − Cl, 65), 423 (M − CHR$_2$ − 2Cl − *t*-Bu −1, 36), 287 (ArP=C − 1, 56), 165 (CHR$_2$, 75), 119 (Mes, 16), 57 (*t*-Bu, 100). Anal. Calcd for C$_{41}$H$_{49}$Cl$_2$GeP: C, 68.75; H, 6.89. Found: C, 68.78; H, 6.92.

Synthesis of ArP=C(Cl)Ge(Mes)(Bu)CHR$_2$ (11). To a solution of **8** (1.00 g, 1.40 mmol) in Et$_2$O/toluene (10 mL/10 mL) cooled to −78 °C was added *n*-BuLi (0.96 mL, 1.6 M in hexane, 1.54 mmol). The brown reaction mixture was stirred for 20 min at −78 °C and then warmed to room temperature. After removal of solvents and addition of pentane (30 mL), the lithium salts were removed by filtration. **11** could not be obtained in pure form by crystallization from various solvents but was identified by its spectroscopic data.

^{1}H NMR: δ 0.35−1.05 (m, 9H, Ge*Bu*), 1.38, 1.43 and 1.50 (3 × 9H, *o*- and *p*-*t*-Bu), 2.32, 2.39 and 2.50 (3 × 3H, *o*- and *p*-Me of Mes), 5.00 (s, 1H, C*H*R$_2$), 6.66 (s, 2H, arom H of Mes), 7.10−7.95 (m, 8H, CR$_2$), 7.44 (d, $^{4}J_{HP}$ = 1.4 Hz, 2H, arom H of Ar). ^{13}C NMR: δ 13.4 (Me of Bu), 19.6 (d, $^{3}J_{CP}$ = 7.4 Hz, CH$_2$-Ge), 21.1 (*p*-Me of Mes), 25.1 (*o*-Me of Mes), 26.5 and 26.9 (*C*H$_2$*C*H$_2$CH$_3$), 31.5 (*p*-C*Me$_3$*), 32.8 (d, $^{4}J_{CP}$ = 6.5 Hz, *o*-C*Me$_3$*), 33.0 (d, $^{4}J_{CP}$ = 6.7 Hz, *o*-C*Me$_3$*), 35.1 (*p*-*C*Me$_3$), 37.9 and 38.0 (*o*-*C*Me$_3$), 42.9 (d, $^{3}J_{CP}$ = 5.2 Hz, *C*HR$_2$), 119.8 and 120.1 (C$_4$C$_5$), 122.0 and 122.1 (*m*-C of Ar), 124.5−126.8 (C$_1$C$_2$C$_3$C$_6$C$_7$C$_8$), 129.5 (*m*-C of Mes), 135.6 (d, $^{1}J_{CP}$ = 67.1 Hz, *ipso*-C of Ar), 138.7−145.6 (*o*- and *p*-C of Mes, C$_{10}$C$_{11}$C$_{12}$C$_{13}$), 150.5 (*p*-C of Ar), 153.5 (*o*-C of Ar), 173.7 (d, $^{1}J_{CP}$ = 91.4 Hz, P=C). ^{31}P NMR: δ 286.4. MS (*m*/*z*): 682 (M − Bu + 1, 3), 573 (M − CHR$_2$, 84), 517 (M − CHR$_2$ − *t*-Bu +1, 37), 461 (M − CHR$_2$ − 2*t*-Bu + 2, 23), 287 (ArP=C − 1, 21), 165 (CHR$_2$, 100), 57 (*t*-Bu, 27).

Synthesis of ArP=C(Cl)Ge(Mes)(F)C(Me)R$_2$ (14). To a solution of **7** (0.68 g, 0.97 mmol) in Et$_2$O (15 mL) cooled to −60 °C was added via syringe *t*-BuLi (0.60 mL, 1.7 M in pentane, 1.02 mmol). The dark red reaction mixture was stirred for 15 min at this temperature and then warmed to −50 °C. One equivalent of Me$_2$SO$_4$ (124 mg) was added. The resulting solution was dark brown. After removal of solvents and addition of pentane (30 mL), the lithium salts were removed by filtration; recrystallization from pentane afforded 0.60 g (87%) of a yellow-orange powder of **14** (mp 166 °C).

^{1}H NMR: δ 1.38 (s, 9H, *p*-*t*-Bu), 1.43 and 1.47 (2s, 2 × 9H, *o*-*t*-Bu), 1.97 (broad s, 6H, *o*-Me of Mes), 2.16 and 2.20 (2s, 2 × 3H, *p*-Me of Mes and C*Me*R$_2$), 6.66 (s, 2H, arom H of Mes), 7.10−8.20 (m, 8H, C*R*$_2$), 7.43 (d, $^{4}J_{HP}$ = 2.0 Hz, arom H of Ar). ^{13}C NMR: δ 20.6 (d, $^{3}J_{CF}$ = 4.2 Hz, *Me*CR$_2$), 21.2 (*p*-Me of Mes), 23.8 (d, $^{4}J_{CF}$ = 5.6 Hz, *o*-Me of Mes), 31.5 (*p*-C*Me$_3$*), 33.0 (d, $^{4}J_{CP}$ = 6.7 Hz, *o*-C*Me$_3$*), 35.2 (*p*-*C*Me$_3$), 37.9 and 38.0 (*o*-*C*Me$_3$), 52.4 (d, $^{2}J_{CF}$ = 10.8 Hz, *C*R$_2$), 120.0 and 120.3 (C$_4$C$_5$), 122.0 and 122.3 (*m*-C of Ar), 124.5−127.2 (C$_1$C$_2$C$_3$C$_6$C$_7$C$_8$), 127.8 (*ipso*-C of Mes), 129.1 (*m*-C of Mes), 134.5 (d, $^{1}J_{CP}$ = 65.6 Hz, *ipso*-C of Ar), 139.8, 139.9, 148.2 and 148.5 (*o*-C and *p*-C of Mes, C$_{10}$C$_{11}$C$_{12}$C$_{13}$), 150.9 (*p*-C of Ar), 153.2 (d, $^{2}J_{CP}$ = 2.2 Hz, *o*-C of Ar), 153.8 (*o*-C of Ar), 166.0 (dd, $^{1}J_{CP}$ = 88.7 Hz, $^{2}J_{CF}$ = 9.0 Hz, P=C). ^{19}F NMR: δ −102.9 (d, $^{3}J_{FP}$ = 27.5 Hz). ^{31}P NMR: δ 303.1 (d, $^{3}J_{PF}$ = 27.5 Hz). MS (*m*/*z*): 714 (M, 20), 695 (M − F, 7), 535 (M − CMeR$_2$, 93), 479 (M − CMeR$_2$ − *t*-Bu + 1, 41), 423 (M − CMeR$_2$ − 2*t*-Bu + 2, 59), 287 (ArP=C − 1, 77), 179 (CMeR$_2$, 92), 57 (*t*-Bu, 100). Anal. Calcd for C$_{42}$H$_{51}$ClFGeP: C, 70.66; H, 7.20. Found: C, 70.85; H, 7.35.

Synthesis of ArP=C(Cl)Ge(Mes)(Cl)C(Me)R$_2$ (15). 15 was obtained by the same process as **14** using (1.23 g, 1.71 mmol) of **8**, *t*-BuLi (1.11 mL, 1.7 M in pentane, 1.89 mmol), and 215 mg of Me$_2$SO$_4$ in THF/Et$_2$O (10 mL/10 mL). A 0.88 g (70%) amount of an orange powder of **15** was obtained by crystallization from pentane (mp 150 °C).

^{1}H NMR: δ 1.39 (s, 9H, *p*-*t*-Bu), 1.44 and 1.52 (2s, 2 × 9H, *o*-*t*-Bu), 2.08 (broad s, 6H, *o*-Me of Mes), 2.24 and 2.26 (*p*-Me of Mes and C*Me*R$_2$), 6.70 (s, 2H, arom H of Mes), 7.20−8.30 (m, 10H, arom H of Ar and CR$_2$). ^{13}C NMR: δ 21.1 and 21.2 (*p*-Me of Mes and C*Me*R$_2$), 24.9 (*o*-Me of Mes), 31.4 (*p*-C*Me$_3$*), 33.2 (d, $^{4}J_{CP}$ = 6.8 Hz, *o*-C*Me$_3$*), 33.4 (d, $^{4}J_{CP}$ = 6.6 Hz, *o*-C*Me$_3$*), 35.1 (*p*-*C*Me$_3$), 37.9 and 38.2 (*o*-*C*Me$_3$), 53.3 (*C*R$_2$), 120.0 and 120.4 (C$_4$C$_5$), 121.8 and 122.5 (*m*-C of Ar), 124.6−127.3 (C$_1$C$_2$C$_3$C$_6$C$_7$C$_8$), 129.5 (*m*-C of Mes), 134.2 (d, $^{1}J_{CP}$ = 68.1 Hz, *ipso*-C of Ar), 139.8−148.4 (*o*- and *p*-C of Mes, C$_{10}$C$_{11}$C$_{12}$C$_{13}$), 150.6 (*p*-C of Ar), 153.2 (d, $^{2}J_{\mathrm{CP}} = 2.5$ Hz, *o*-C of Ar), 154.4 (*o*-C of Ar), 165.8 (d, $^{1}J_{\mathrm{CP}} = 92.4$ Hz, $\mathrm{P{=}C}$). ^{31}P NMR: δ 294.7. MS (*m*/*z*): 551 (M − $\mathrm{CMeR_2}$, 7), 515 (M − $\mathrm{CMeR_2}$ − Cl − 1, 5), 459 (M − $\mathrm{CMeR_2}$ − Cl − *t*-Bu + 1, 6), 287 ($\mathrm{ArP{=}C}$ − 1, 39), 179 ($\mathrm{CMeR_2}$, 26), 57 (*t*-Bu, 100). Anal. Calcd for $\mathrm{C_{42}H_{51}Cl_2GeP}$: C, 69.07; H, 7.04. Found: C, 69.21; H, 7.26.

Synthesis of $\mathrm{ArP{=}C(Cl)Ge(Mes)(OMe)CHR_2}$ (20). To a solution of **7** (1.08 g, 1.54 mmol) in THF (15 mL) cooled to −100 °C was added *n*-BuLi (1.00 mL, 1.6 M in hexane, 1.54 mmol). To the black-brown resulting solution was added at −100 °C after 20 min of stirring a slight excess of methanol. The reaction mixture became immediately light orange. After the usual workup, **20** was recrystallized from pentane as white crystals (mp 189 °C).

^{1}H NMR: δ 1.31 (s, 9H, *p*-*t*-Bu), 1.33 (s, 18H, *o*-*t*-Bu), 2.24 (s, 3H, *p*-Me of Mes), 2.31 (s, 6H, *o*-Me of Mes), 3.44 (s, 3H, OMe), 4.76 (broad s, 1H, C*H*R$_2$), 6.77 (s, 2H, arom H of Mes), 7.11−7.92 (m, 8H, $\mathrm{CR_2}$), 7.35 (d, $^{4}J_{\mathrm{HP}} = 1.5$ Hz, 2H, arom H of Ar). ^{13}C NMR: δ 21.2 (*p*-Me of Mes), 23.9 (*o*-Me of Mes), 31.5 (*p*-C*Me*$_3$), 33.0 (d, $^{4}J_{\mathrm{CP}} = 6.3$ Hz, *o*-C*Me*$_3$), 33.1 (d, $^{4}J_{\mathrm{CP}} = 6.6$ Hz, *o*-C*Me*$_3$), 35.1 (*p*-*C*Me$_3$), 37.8 and 37.9 (*o*-*C*Me$_3$), 43.6 (d, $^{3}J_{\mathrm{CP}} = 3.5$ Hz, *C*HR$_2$), 54.0 (OMe), 120.0 and 120.1 ($\mathrm{C_4C_5}$), 122.0 and 122.2 (*m*-C of Ar), 125.2−126.6 ($\mathrm{C_1C_2C_3C_6C_7C_8}$), 129.4 (*m*-C of Mes), 134.7 (d, $^{1}J_{\mathrm{CP}} = 67.6$ Hz, *ipso*-C of Ar), 139.7−144.4 (*o*-C and *p*-C of Mes, $\mathrm{C_{10}C_{11}C_{12}C_{13}}$), 150.6 (*p*-C of Ar), 153.4 (d, $^{2}J_{\mathrm{CP}} = 2.3$ Hz, *o*-C of Ar), 153.6 (d, $^{2}J_{\mathrm{CP}} = 2.1$ Hz, *o*-C of Ar), 166.7 (d, $^{1}J_{\mathrm{CP}} = 91.3$ Hz, $\mathrm{P{=}C}$). ^{31}P NMR: δ 299.2. MS (*m*/*z*): 677 (M − Cl, 3), 589 (M − Cl − OMe − *t*-Bu, 2), 547 (M − $\mathrm{CHR_2}$, 37), 515 (M − $\mathrm{CHR_2}$ − OMe − 1, 35), 459 (M − $\mathrm{CHR_2}$ − *t*-Bu − OMe, 17), 287 ($\mathrm{ArP{=}C}$ − 1, 41), 165 ($\mathrm{CHR_2}$, 100), 57 (*t*-Bu, 85). Anal. Calcd for $\mathrm{C_{42}H_{52}ClGeOP}$: C, 70.86; H, 7.36. Found: C, 70.92; H, 7.45.

Synthesis of Dimer 2. To a solution of **7** (1.10 g, 1.57 mmol) in $\mathrm{Et_2O}$ (15 mL) cooled to −60 °C was added *t*-BuLi (1 mL, 1.7 M in pentane, 1.70 mmol). When the resulting red-brown mixture was warmed to room temperature, no change was observed. A ^{31}P NMR spectrum displayed the signal of **12** (δ 295.71 ppm, d, $^{3}J_{\mathrm{PF}} = 18.8$ Hz). **12** was recovered almost unchanged after 1 h in refluxing $\mathrm{Et_2O}$, since only ∼10% of **2** was formed. The solution of **12** was cooled again to −50 °C, and 1 equiv of $\mathrm{Me_3SiCl}$ (0.17 g) was added. The reaction mixture was then warmed to room temperature; the solvents were removed in vacuo and replaced by pentane (30 mL). After removal of lithium salts, **2** was recrystallized from pentane to afford 1.46 g (75%) of yellow crystals (mp 270 °C).

^{1}H NMR (200 MHz): δ 0.87 (s, 6H, *o*-Me of Mes), 1.26 (s, 18H, *p*-*t*-Bu), 1.28 (s, 36H, *o*-t-Bu), 2.15 (s, 6H, *p*-Me of Mes), 3.05 (s, 6H, *o*-Me of Mes), 6.25 and 6.77 (2s, 2 × 2H, arom H of Mes), 6.54, 6.92, 6.92, and 7.21 (4t, $^{3}J_{\mathrm{HH}} = 7.1$ Hz, 4 × 2H, H on $\mathrm{C_2C_3C_6C_7}$), 6.75, 7.25, 7.43, and 8.16 (4d, $^{3}J_{\mathrm{HH}} = 7.1$ Hz, 4 × 2H, H on $\mathrm{C_1C_4C_5C_8}$). ^{13}C NMR: δ 21.0 (*p*-Me of Mes), 24.0 and 28.0 (*o*-Me of Mes), 31.4 (*p*-C*Me*$_3$), 32.8 and 33.0 (2d, $^{4}J_{\mathrm{CP}} = 7.2$ Hz, *o*-C*Me*$_3$), 35.0 (*p*-*C*Me$_3$), 37.7 and 37.8 (*o*-*C*Me$_3$), 72.3 (d, $^{3}J_{\mathrm{CP}} = 4.5$ Hz, *C*R$_2$), 117.8 and 118.6 ($\mathrm{C_4C_5}$), 121.9 (*m*-C of Ar), 124.5−128.7 ($\mathrm{C_1C_2C_3C_6C_7C_8}$, *m*-C of Mes), 135.8 (d, $^{1}J_{\mathrm{CP}} = 71.0$ Hz, *ipso*-C of Ar), 137.4−150.4 (*o*- and *p*-C of Mes, *p*-C of Ar, $\mathrm{C_{10}C_{11}C_{12}C_{13}}$), 153.4 and 153.5 (*o*-C of Ar), 173.1 (d, $^{1}J_{\mathrm{CP}} = 96.4$ Hz, $\mathrm{P{=}C}$). ^{31}P NMR: δ 304.8. MS (*m*/*z*): 328 ($\mathrm{R_2C{=}CR_2}$, 45), 165 ($\mathrm{CHR_2}$, 18), 57 (*t*-Bu, 100). Anal. Calcd for $\mathrm{C_{82}H_{96}Cl_2Ge_2P_2}$: C, 72.44; H, 7.12. Found: C, 72.51; H, 7.26.

Crystal Structure Determination. The data were collected on a MAR345 image plate with graphite-monochromated Mo Kα radiation. The structure was solved by direct methods and refined using the program SHELX-97.[22] Hydrogen atoms were placed in calculated positions, and all other atoms were refined with anisotropic thermal parameters. Since each of the two independent molecules in the asymmetric unit is a dimer, there are four chemically equivalent "monomers" in the asymmetric unit. Restraints with a standard deviation of 0.02 Å were applied to equivalent bond distances (1−2 distances) and angles (1−3 distances) between the four "monomers". The largest residual densities are close to the germanium atoms.

Supporting Information Available: Listings of atomic coordinates, anisotropic displacement parameters, bond distances and angles, and torsion angles and stereoviews of **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

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