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Unsaturated Germanium and Phosphorus Compounds: Reactions of Germaphosphenes with α-Ethylene Aldehydes and Ketones

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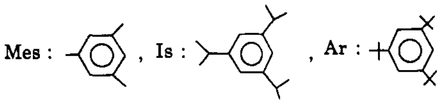
Germaphosphenes Mes$_2$Ge=PR (R: 2,4,6-triisopropylphenyl (Is), **1**; 2,4,6-tri-*tert*-butylphenyl (Ar), **2**) react with α-ethylene aldehydes and ketones to give [2 + 2] and [2 + 4] cycloadditions (for aldehydes) and [2 + 4] cycloadditions and 1,2-additions (for ketones). Four- and six-membered ring derivatives can be easily differentiated by ^{31}P NMR chemical shifts which are, respectively, +36 to +89 ppm and −33 to −77 ppm. **5a′**, obtained from **2** and crotonaldehyde, has been structurally characterized by X-ray diffraction: the six-membered ring (germaoxaphosphorinene) conformation is a sofa form, with large folding along the Ge—C axis. A NMR study at various temperatures for **3a**, **3a′**, and **5a′** displays dynamic phenomenon including phosphorus and ring inversion. The low ΔG^* values (respectively 18.2, 13.7, and 13.2 kcal/mol) seem mainly due to substitution of phosphorus by the electropositive germanium and particularly to large steric effects; the 2,4,6-tri-*tert*-butylphenyl group lowers the inversion barrier by 5 kcal/mol when compared with the 2,4,6-triisopropylphenyl group.

Introduction

Stable sila-, germa-, and stannaphosphenes >M=P– (M: Si,[1] Ge[2,3] Sn[4,5]) were synthesized some years ago and their chemical behavior is now rather well-known. However only cycloadditions with sulfur,[1b,3d] selenium,[1b] tellurium,[1b] benzaldehyde,[3c] and α-phenyl *N*-*tert*-butyl nitrone[3c] have been described so far. In this paper we describe the reactivity of germaphosphenes **1**[3c] and **2**[3a] toward α-ethylene aldehydes and ketones.

Mes$_2$Ge=PIs   Mes$_2$Ge=PAr

1   **2**



All the reactions were performed with these two stable germaphosphenes showing different steric hindrance, in order to determine the effect on the course of the reaction of the bulkiness of the aryl group attached to phosphorus.

1 and **2** were allowed to react with acrolein, methacrolein, crotonaldehyde, and 3-methyl-2-butenal as representatives of α,β-unsaturated aldehydes and with methyl vinyl ketone, methyl isopropenyl ketone, and mesityl oxide as typical α,β-unsaturated ketones. The reactions were run at room temperature with reagents in an equivalent molar ratio. The adducts were characterized by ^{1}H, ^{13}C, and ^{31}P NMR spectroscopy and other analytical methods such as IR, mass spectroscopy, or elemental analysis and, in one case, by X-ray diffraction, in order to confirm the structure assigned on the basis of NMR spectroscopy.

Results and Discussion

Many types of reaction could a priori be possible between germaphosphenes and α-ethylene aldehydes and ketones; among the most likely are (1) a [2 + 4] cycloaddition in two possible regiochemistries (oxygen bonded to germanium or to phosphorus), (2) a [2 + 2] cycloaddition with the C=O or C=C unsaturations, in which cases two regiochemistries are also possible, (3) a reaction with the enolic form of ketones, and (4) an ene reaction with the allylic hydrogen in some aldehydes and ketones.

In fact, three of these routes have been observed, depending on the germaphosphene and the aldehyde or ketone employed. Our results are presented in schemes I and II.

With aldehydes (Scheme I), only [2 + 2] and [2 + 4] cycloadditions were observed; the ratio four-membered ring (germaoxaphosphetanes)/six-membered ring (germaoxaphosphorinenes) cycloadduct is highly dependent on the steric requirements of the reactants. With the less hindered germaphosphene **1**, six-membered ring derivatives were obtained exclusively, except with 3-methyl-2-

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(1) (a) Smit, C. N.; Lock, F. M.; Bickelhaupt, F. *Tetrahedron Lett.* **1984**, *25*, 3011. (b) Van der Winkel, Y.; Bastiaans, H. M. M.; Bickelhaupt, F. *J. Organomet. Chem.* **1991**, *405*, 183. (c) Smit, C. N.; Bickelhaupt, F. *Organometallics* **1987**, *6*, 1156. (d) Corriu, R.; Lanneau, G.; Priou, C. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 1130. (e) Driess, M. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 1022.

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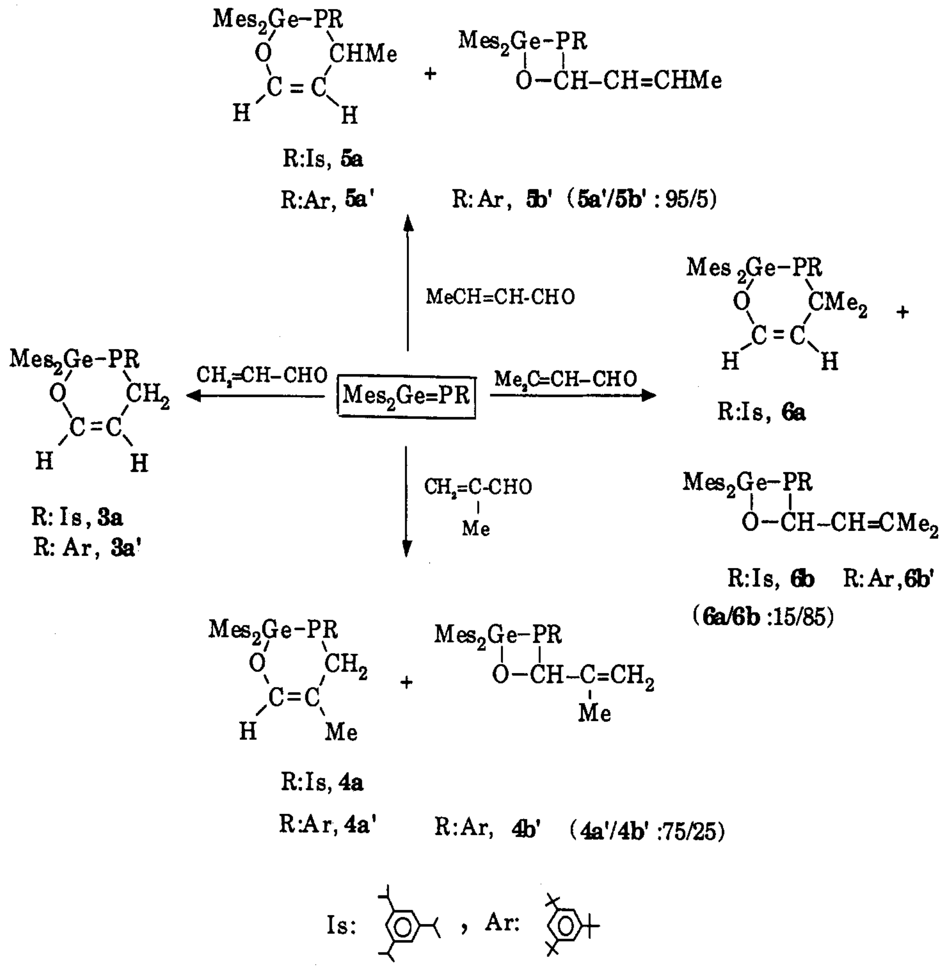
Scheme I. Reactions of Germaphosphenes 1 and 2 with α-Ethylene Aldehydes[a]



[a] All the products obtained from the same aldehyde have the same number. Six-membered rings are labeled **a** (R: Is) or **a′** (R: Ar). Four-membered rings are labeled **b** (R: Is) or **b′** (R: Ar).

butenal, in which case the germaoxaphosphetane **6b** was the major product. With germaphosphene **2**, which has the very bulky 2,4,6-tri-*tert*-butylphenyl group on phosphorus, the germaoxaphosphetanes were obtained in three cases, and even exclusively with 3-methyl-2-butenal.

With ketones (Scheme II), both germaoxaphosphorinenes and open-chain products, resulting from a reaction with the enolic form of the ketones, were obtained; as in the case of aldehydes, steric hindrance determines the course of the reaction since with mesityl oxide, which has two methyl groups on the β-carbon, only open-chain products were formed, whereas with methyl vinyl ketone, six-membered ring derivatives were obtained. In the reaction of methyl isopropenyl ketone with the germaphosphene **1**, the formation of the six-membered ring compound **8a** was observed exclusively. The corresponding reaction with **2**, which is substituted on phosphorus by a bulkier group than **1**, gave six-membered ring **8a′** and open-chain **8c′** (in a minor ratio) compounds.

The results summarized in Schemes I and II and Table I show that six- and four-membered ring compounds are obtained with aldehydes and that four-membered ring derivatives and open-chain products are formed with ketones. [2 + 2] cycloadditions to the C=C double bond and ene reactions involving the allylic hydrogen of the methyl group on the ethylene double bond have never been observed nor has the reverse regiochemistry involving the formation of derivatives with oxygen bonded to phosphorus. Although compounds with a germanium—phosphorus single bond, for example the germylphosphane $Et_3Ge—PEt_2$, react with α-ethylene aldehydes and ketones to give 1,4-additions,[6] we have never observed a reaction of the carbonyl compound with the Ge—P single bond of our adducts, probably due to the very large steric hindrance around this bond.

(a) Proposed Mechanism. In the [2 + 2] and [2 + 4] cycloadditions, we have observed only one type of regiochemistry, with oxygen bonded to germanium. This regiochemistry is strongly influenced by the well-known affinity of germanium for oxygen, and the polarities of the reactants, i.e. $Ge^{\delta+}{=}P^{\delta-}$ and $C^{\delta+}{=}C^{\delta-}{-}C^{\delta+}{=}O^{\delta-}$. For these reasons the first step of the reaction could be nucleophilic attack of oxygen on germanium followed by nucleophilic attack of phosphorus on the β-carbon, leading to six-membered rings. With aldehydes which have the β-carbon substituted by one or two methyl groups, as in crotonaldehyde and 3-methyl-2-butenal, the second attack required to close the ring is difficult, particularly in the case of germaphosphene **2** having the very bulky Ar group; therefore phosphorus attacks the carbon of the carbonyl group, leading to four-membered rings.

With ketones such as mesityl oxide, where the α-carbon is also substituted by a methyl group, ring closure is not easy due to steric hindrance, and a different reaction occurs, involving the enolic form of the carbonyl derivative.

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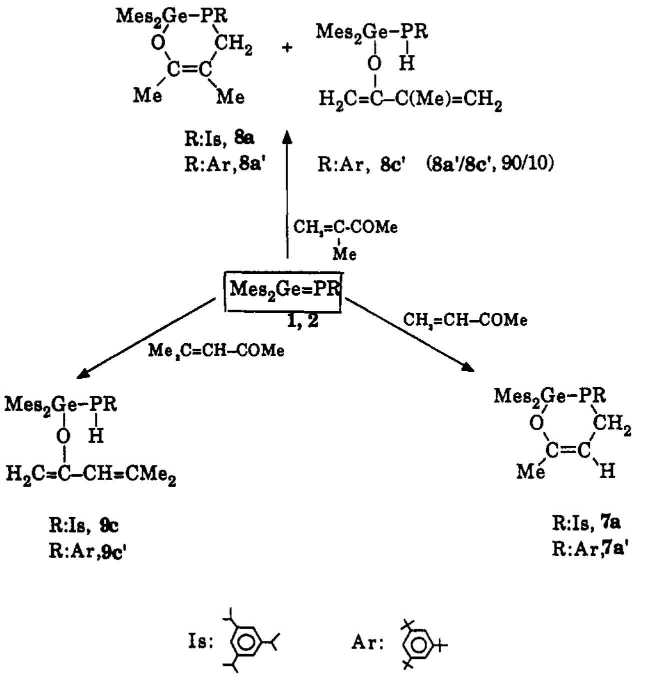
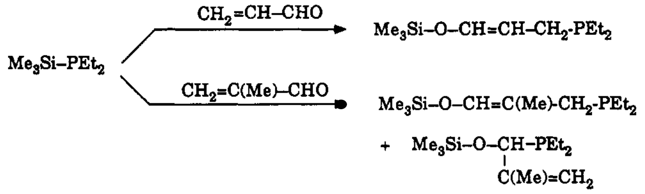
Scheme II. Reactions of Germaphosphenes 1 and 2 with α-Ethylene Ketones



[a] All the products obtained from the same ketone have the same number. Six-membered rings are labeled **a** (R: Is) or **a′** (R: Ar). Open-chain products are labeled **c** (R: Is) or **c′** (R: Ar).

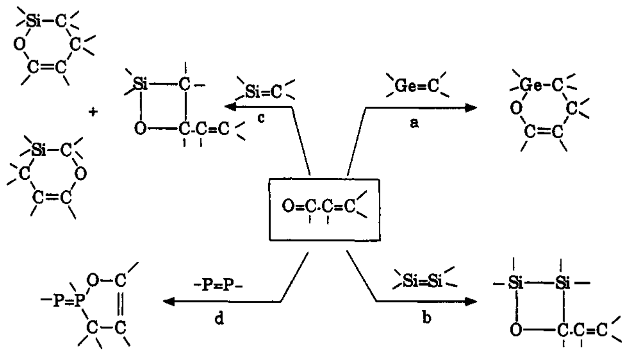
Scheme III



The formation of the four-membered ring compound **4b′** (even in minor amount: 25%) with methacrolein seems surprising because there is no steric hindrance on the β-carbon: thus, only a [2 + 4] cycloaddition should occur. A similar result has been reported in the reactions of silylphosphane Me_3SiPEt_2 with various α-ethylene aldehydes: whereas 1,4-addition to the silicon–phosphorus single bond was observed exclusively with crotonaldehyde, both 1,2- and 1,4-additions occurred with methacrolein[6] (Scheme III). These results were explained using the hard and soft acid and base theory of Pearson: in the case of crotonaldehyde, the soft phosphorus preferentially reacts with the β-carbon which is softer than the carbon of carbonyl, whereas with methacrolein phosphorus can react with either of these two carbon atoms which differ slightly in softness. In our case this theory can also explain the formation of **4b′**.

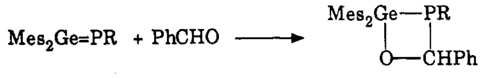
(b) Reactions Observed with Other Doubly-Bonded Main Group Elements. Various types of reactions have been observed between α-ethylene aldehydes or ketones and other doubly-bonded main group elements: exclusive [2 + 2] cycloadditions occur with disilenes,[7] [2 + 4] with germenes,[8] [2 + 2] and [2 + 4] (in both regiochemistries in this last case) with silenes,[9] whereas with diphosphenes, a cycloaddition was observed involving one of the phosphorus atoms to give a five-membered ring.[10] These results, which are very different from those observed with germaphosphenes, are summarized in Scheme IV:

Scheme IV. Reactions of α-Ethylene Aldehydes and Ketones with Various Doubly-Bonded Main Group Elements



NMR Studies

(a) ^{31}P NMR Spectra. ^{31}P NMR spectra allow the immediate identification of compounds because four- and six-membered rings have very different chemical shifts in the range +36 to +89 ppm for germaoxaphosphetanes, and −33 to −77 ppm for germaoxaphosphorinenes (see Table I). Whereas chemical shifts appear at the expected field for a phosphorus atom bonded to germanium in a six-membered ring, four-membered ring compounds **4b′**, **5b′**, **6b**, and **6b′** have chemical shifts at much lower field, as has already been observed in germaoxaphosphetane analogs **10** obtained in the [2 + 2] cycloaddition of germaphosphene **1** or **2** with benzaldehyde:[3c]



10

R : Is, $\delta^{31}P$: + 45.6 ppm

R : Ar, $\delta^{31}P$: + 82.5 ppm

These unexpected chemical shifts could be due to folding of the ring along the Ge–C axis, allowing an interaction between phosphorus and oxygen lone pairs and thereby causing greater deshielding in heterocycles **4b′**, **5b′**, and **6b′** (δ between +77.61 and +89.06 ppm) than in **6b** (δ: +36.45 ppm). In **4b′**, **5b′**, and **6b′**, phosphorus is substituted by the very bulky 2,4,6-tri-*tert*-butylphenyl group, and due to the greater steric hindrance of the Ar group, the four-membered ring might undergo a greater folding. However, single crystal X-ray structures are necessary to test this idea.

Germylphosphanes **8c′**, **9c**, and **9c′** are easily identified by ^{31}P NMR spectra: they show the expected $^1J_{PH}$ coupling constant (~200 Hz) for a P(III) derivative. As in the case of four-membered ring compounds, chemical shifts for six-membered ring adducts obtained from **1** are at a higher field than those obtained from **2**.

(b) ^{13}C NMR Spectra. ^{13}C NMR spectra are also useful in differentiating between four- and six-membered ring compounds: the sp^2 carbon bonded to oxygen was observed

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[7] Fanta, A. D.; Young, D. J.; Belzner, J.; West, R. *Organometallics* **1991**, *10*, 3466.

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[10] Weber, L.; Frebel, M.; Boese, R. *Organometallics* **1989**, *8*, 1718.

Table I. $\delta(^{31}P)$ **(ppm) and Ratios of Adducts in Parentheses (Solvent $CDCl_3$) ($^1J_{PH}$ Values in Hertz)**

	$CH_2=$ CH—CHO	$CH_2=$ C(Me)—CHO	Me—CH= CH—CHO	$Me_2C=$ CH—CHO	$CH_2=$ CH—COMe	$CH_2=$ C(Me)—COMe	$Me_2C=$ CH—COMe
				$Mes_2Ge=PIs$			
[2 + 4]	–76.82 (100) [**3a**]	–75.78 (100) [**4a**]	–58.15 (100) [**5a**]	–61.36 (15) [**6a**]	–75.51 (100) [**7a**]	–70.96 (100) [**8a**]	
[2 + 2]				+36.45 (85) [**6b**]			
open product							–141.97 (100), $^1J_{PH}$:206 [**9c**]
				$Mes_2Ge=PAr$			
[2 + 4]	–56.34 (100) [**3a′**]	–58.24 (75) [**4a′**]	–33.77 (95)[a] [**5a′**]		–57.10 (100) [**7a′**]	–56.00 (90) [**8a′**]	
[2 + 2]		+77.61 (25) [**4b′**]	+89.06 (5) [**5b′**]	+80.86 (100) [**6b′**]			
open product						–104.70 (10), $^1J_{PH}$:205 [**8c′**]	–100.29 (100), $^1J_{PH}$:214 [**9c′**]

[a] –30.90 in C_7D_8.

at low field (~147–150 ppm) in the six-membered ring derivatives, whereas the sp^3 carbon of germaoxaphosphetanes appeared, as expected, at a higher field (for example 83.62 ppm in **6b′** and 92.12 in **4b′**). The germaoxaphosphorinene structure was also demonstrated by the existence of a $^1J_{PC}$ coupling constant (25–33 Hz) between the β-carbon and the phosphorus atom.

In some compounds, particularly **5a′** and **8a′**, broad signals were observed for carbon atoms of 2,4,6-tri-*tert*-butylphenyl and mesityl groups: this is due to the very large steric hindrance which causes their hindered rotation. When the α- and β-carbon atoms of the starting carbonyl derivative are substituted only by hydrogen atoms (acrolein, methyl vinyl ketone), hindered rotation is not observed.

(c) ^{1}H NMR Spectra. In ^{1}H NMR spectra of many compounds, signals of mesityls, Is, and Ar groups are extremely broad, and sometimes are even unobservable. This is due both to very large steric hindrance, which prevents free rotation of such groups, and also to phosphorus inversion: at 25 °C (the temperature of the NMR probe) the signals almost coalesce. However, good NMR spectra with sharp signals were obtained in some cases, particularly when the group on phosphorus was a triisopropylphenyl.

For compounds **3a**, **5a**, **5a′**, and **7a** we observed, as expected, two inequivalent mesityl groups. In contrast, the mesityl groups and the two hydrogens of the CH_2P moiety of **3a′** are equivalent, which can only be explained by a rapid inversion at phosphorus (see further).

In ^{1}H and ^{13}C NMR of compounds **a**, which have the phosphorus atom substituted by a 2,4,6-triisopropylphenyl group, the two methyls of an isopropyl group are theoretically inequivalent; this is confirmed by the spectra which display two doublets (^{1}H NMR) or two singlets (^{13}C NMR) for the methyls of *o*-isopropyl groups. But, probably due to the distance of chiral phosphorus, the methyls of *p*-isopropyl groups give only one doublet (^{1}H NMR) or one singlet (^{13}C NMR).

Compound **5a′**, which has been unambiguously characterized by X-ray diffraction, possesses two chiral atoms (phosphorus and the carbon substituted by a methyl and a hydrogen) and should exist as a mixture of diastereoisomers. However, at room temperature only one signal was observed in its ^{31}P NMR spectrum. Once again, this can only be explained by rapid inversion at phosphorus (see later).

In contrast, phosphorus inversion does not occur in **5a** at room temperature, as evident from the inequivalence of the two mesityl groups, but we have not been able to determine the configuration of phosphorus by examination of the $^2J_{PCH}$ coupling constant: because of coupling with the two ethylene hydrogens, the methyl and the phosphorus, the hydrogen of the CHMe moiety appeared as a complex multiplet and it was not possible, even at 250 MHz, to determine its coupling constant with phosphorus.

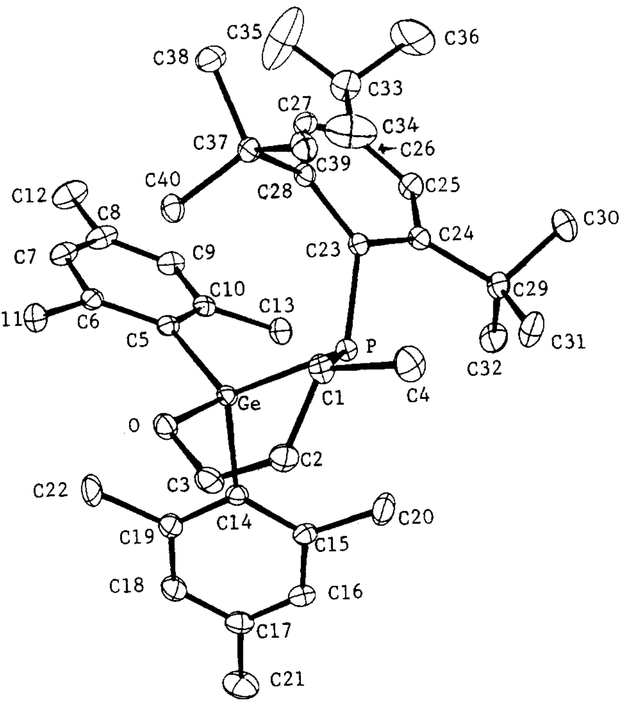


Figure 1. ORTEP drawing of **5a′** showing the thermal ellipsoids at the 20% probability level. Hydrogen atoms are omitted for clarity.

In four-membered heterocycles, the formation of only one diastereoisomer was always observed. In such highly strained heterocycles, rapid phosphorus inversion could not occur and it is reasonable to suppose that we obtained exclusively the diastereoisomer with the aryl group on phosphorus and the hydrogen on the adjacent carbon in a cis arrangement.

(d) Inversion Barrier at Phosphorus. In order to determine the effect of steric factors on the inversion barrier at phosphorus, we have studied **3a**, **3a′**, and **5a′** by dynamic ^{1}H and ^{31}P NMR spectroscopy. The only difference between **3a** and **3a′** is the substituent on phosphorus (Is or Ar), and between **3a′** and **5a′** it is the substituent on the carbon bonded to phosphorus (Me or H).

Phosphorus inversion is proved unambiguously by two facts: (1) mesityl groups bonded to germanium in **3a** and **3a′** are inequivalent (one Mes cis to the aryl group on phosphorus, the other one cis to the phosphorus lone pair)

Table II

	3a			3a′		
	T_c (K)	$\delta\nu$ (Hz)	ΔG^* (kcal/mol)	T_c (K)	$\delta\nu$ (Hz)	ΔG^* (kcal/mol)
o-Me	374	78.1	18.21	271	45.5	13.25
p-Me	351	13.93	18.24	249	6.5	13.15
H arom Mes	361	29.79	18.24			
			18.2 (av)			13.2 (av)

at low temperature but become equivalent when the temperature increases and (2) in **5a′**, there are at -40 °C two diastereoisomers (both C and P are chiral) which change to only one diastereoisomer at room temperature. These phenomena cannot be due to a cyclohexene type inversion: in a change of conformation (from one sofa form to another) mesityls cannot become equivalent and there would be still two diastereoisomers in the case of **5a′**, as the phosphorus atom remains chiral in this ring inversion; however, such cyclohexene type inversion probably occurs in these derivatives since its magnitude is usually small.

Rapid inversion of phosphorus occurs at room temperature in **3a′**, but not in **3a**, as demonstrated by the inequivalence of mesityl groups on germanium. In the case of **3a′**, the very bulky 2,4,6-tri-*tert*-butylphenyl group increases the phosphorus pyramid angle and thereby decreases the inversion barrier. In the case of **3a** and **3a′** the dynamic NMR study (solvent C_7D_8) was done using ^1H NMR spectra. For **3a′**, we followed the coalescence of *o*- and *p*-methyl signals of mesityl groups. For **3a** we observed the coalescence of these signals, and also those of aromatic protons of the mesityls (see Table II). The inversion barrier was calculated by the Eyring equation.

The inversion barrier at phosphorus in **3a** (18.2 kcal/mol) is 5 kcal/mol higher than that in **3a′** (13.2 kcal/mol). The only difference between **3a** and **3a′** is the bulkiness of substituent on phosphorus, since the two groups 2,4,6-tri-*tert*-butylphenyl and 2,4,6-triisopropylphenyl have similar electronic properties. Thus, the 5 kcal/mol difference in ΔG^* between **3a** and **3a′** can only be due to steric effects. It appears once more that the Ar group is extremely bulky, as also evident in its great stabilizing power in low coordinated species, and much bulkier than the Is group.

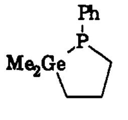
Since **5a′** possesses two chiral centers (P and C bonded to phosphorus), phosphorus inversion could not be followed by ^1H NMR measurements: even in the case of rapid inversion at phosphorus, the two mesityl groups are inequivalent due to the chiral carbon of the crotonaldehyde moiety. Therefore phosphorus inversion was studied by dynamic ^{31}P NMR spectroscopy.

At -40 °C, two signals (-32.70 and -55.03 ppm, ratio 90/10, solvent C_7D_8), corresponding to the two diastereoisomers, were observed as expected. The coalescence temperature occurred at approximately 54 °C. Thus the inversion barrier at phosphorus was calculated to be about 13.7 kcal/mol. However, the value of ΔG^* in this case is not entirely satisfactory because the ratio of the starting diastereoisomers was not 50/50.

The main factors affecting the magnitude of inversion barriers are steric effects, effects of conjugation, angular constriction, and heteroatomic substitution, particularly the electronegativity of substituents.[11]

In compounds **3a**, **3a′**, and **5a′**, steric effects play a major role in lowering the phosphorus inversion barrier. Conjugation between the phosphorus lone pair and the aromatic ring on phosphorus is also important, but the other determining factor is probably the substitution of phosphorus by the electropositive germanium (electronegativity ~2.0),[12] since it is well-known that group 14 elements bonded to phosphorus lower its inversion barrier.[13]

Our results are consistent with values of ΔG^* for cyclic germylphosphanes: for example 24.3[13a] and 18.5[13b] kcal/mol, respectively, for the five-membered rings **11** and **12** in which groups attached to germanium and phosphorus have low steric requirements.



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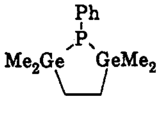
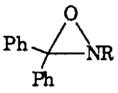


12

(R: Me, tBu)

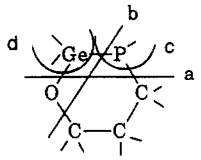


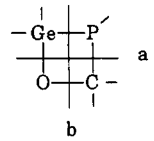
13

The difference observed for the ΔG^* between **3a** and **3a′** (5 kcal/mol) is not surprising since the inversion barrier of pyramidal atoms such as N or P is highly dependent on steric hindrance. For example, in diphenyloxaziridine **13** the activation energy for pyramidal inversion of the methyl derivative is 6.4 kcal/mol higher than the inversion barrier of the *tert*-butyl derivative.[11a]

Mass Spectroscopy

For six-membered ring compounds, the most important fragmentation leads to the starting material (route a). However, we have observed three other types of





fragmentation: b (formation of germanone and of the P—C—C=C moiety), c (release of phosphinidene), and d (release of germylene). In the four-membered ring compounds (for example **6b′**) the two classical fragmentations of four-membered ring heterocycles, a and b, are observed, but b, leading in particular to germanone $Mes_2Ge{=}O$, is the most important. The same fragmentations a and b have been observed in the [2 + 2] cycloadducts between **1** or **2** and benzaldehyde.[3c]

X-ray Structural Determinations (See Tables III–V)

The bulky 2,4,6-tri-*tert*-butylphenyl and mesityl groups have a pronounced steric effect on the molecule, resulting in some bond angles deviating from those expected. For example angles P–Ge–C(14) (115.9(1)°) and P–Ge–C(5) (118.6(1)°) are significantly wider than expected, while

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Table III. Crystal Structure Data for 5a′

formula	$C_{40}H_{57}OPGe$
M_r	657.43
cryst dimens, mm^3	0.6 × 0.3 × 03
cryst syst	triclinic
space group	$P\bar{1}$
a, Å	9.684(2)
b, Å	12.453(2)
c, Å	16.904(2)
α, deg	72.90(1)
β, deg	88.85(2)
γ, deg	72.81(2)
V, Å^3	1856.3(5)
Z	2
d_{calcd}, g/cm^3	1.18
μ(Mo Kα), mm^{-1}	0.93
F(000)	704
T, °C	room temperature
hkl range	−11/+11, −14/15,0/20
no. of rflns	
measd	7281
obsd (>2.5 $\sigma(I)$)	5825
s (goodness of fit)	1.94
Δ/σ max	<1
R^a	0.060
R_w	0.066
w (wheighting scheme)	$1/(\sigma^2(F) + 0.0010F^2)$
$\Delta\rho$ final (max/min), e/Å^3	0.97/−0.81

Table IV. Selected Interatomic Distances (Å), Angles (deg), and Torsion Angles (deg) in the Crystal Structure of 5a′

Bond Distances			
P–Ge	2.371(1)	O–Ge	1.832(3)
P–C(1)	1.888(5)	Ge–C(5)	1.957(5)
C(1)–C(2)	1.484(6)	Ge–C(14)	2.003(5)
C(2)–C(3)	1.344(7)	P–C(23)	1.861(4)
C(3)–O	1.357(7)	C(1)–C(4)	1.528(7)
Bond Angles			
C(5)–Ge–O	110.5(1)	C(1)–P–Ge	97.8(1)
P–Ge–O	100.1(1)	C(23)–P–Ge	109.2(1)
P–Ge–C(14)	115.9(1)	C(1)–C(23)	116.2(2)
P–Ge–C(5)	118.6(1)	P–C(1)–C(2)	108.9(3)
O–Ge–C(14)	100.0(2)	C(1)–C(2)–C(3)	125.6(5)
C(14)–Ge–C(5)	109.6(2)	C(2)–C(3)–O	122.7(4)
Torsion Angles			
O–Ge–P–C(1)	0	C(5)–Ge–P–C(23)	0
Ge–P–C(1)–C(2)	46	C(23)–P–C(1)–C(4)	−79
P–Ge–O–C(3)	−51	C(1)–C(2)–C(3)–O	4
Distances to the Mean Plane C(23),C(24),C(25),C(26),C(27),C(28)			
C(23)	+0.11	C(26)	+0.09
C(24)	−0.07	C(27)	−0.04
C(25)	−0.03	C(28)	−0.06
Distances to the Mean Plane Ge-P-C(1)-C(2)-C(3)-O			
Ge	−0.15	C(2)	−0.32
P	−0.16	C(3)	−0.27
C(1)	+0.44	O	+0.45

angles P–Ge–O (100.1(1)°) and O–Ge–C(14) (100.0(2)°) are smaller than normal.

Steric hindrance is also responsible for P–Ge bond (2.371(1) Å; generally 2.33–2.35 Å)[14] elongation and Ge–Mes bond (Ge–C(14): 2.003(5) Å) lengthening while the other Ge–Mes bond lies in the normal range (Ge–C(5): 1.957(5) Å).[15]

Table V. Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Thermal Parameters (Å^2) for 5a′ with Esd's in Parentheses

	x/a	y/b	z/c	B_{eq}
Ge	−2666(1)	5064(1)	−2381(1)	2.4
P	−3934(1)	6156(1)	−3692(1)	2.4
O	−794(3)	4813(3)	−2677(2)	3.3
C(1)	−2308(5)	6140(4)	−4330(3)	3.1
C(2)	−1271(5)	4932(5)	−4076(3)	3.7
C(3)	−571(5)	4357(4)	−3322(3)	3.7
C(4)	−2793(6)	6523(5)	−5251(3)	4.3
C(5)	−2958(5)	5797(4)	−1488(3)	2.8
C(6)	−1873(5)	6087(4)	−1110(3)	3.1
C(7)	−2274(7)	6595(4)	−467(3)	4.1
C(8)	−3607(8)	6804(5)	−179(3)	4.7
C(9)	−4664(6)	6498(5)	−548(3)	4.0
C(10)	−4323(5)	6008(4)	−1199(3)	2.9
C(11)	−310(6)	5884(5)	−1335(3)	4.1
C(12)	−3972(9)	7330(6)	527(4)	6.4
C(13)	−5540(5)	5716(5)	−1571(3)	3.9
C(14)	−2703(5)	3395(4)	−1935(3)	2.9
C(15)	−3579(6).	2882(4)	−2275(3)	3.3
C(16)	−3505(6)	1720(4)	−1898(3)	3.8
C(17)	−2625(6)	1013(4)	−1214(4)	4.2
C(18)	−1737(7)	1498(5)	−892(4)	4.8
C(19)	−1784(6)	2668(4)	−1235(3)	3.9
C(20)	−4622(9)	3549(6)	−3040(4)	6.7
C(21)	−2609(9)	−249(5)	−821(5)	6.8
C(22)	−738(8)	3110(6)	−825(5)	7.0
C(23)	−5073(4)	7627(4)	−3648(3)	2.5
C(24)	−6591(5)	7752(4)	−3674(3)	2.8
C(25)	−7494(5)	8443(5)	−3264(3)	3.5
C(26)	−7033(5)	9118(4)	−2868(3)	3.5
C(27)	−5668(5)	9207(4)	−3005(3)	3.3
C(28)	−4673(4)	8520(4)	−3393(3)	2.6
C(29)	−7403(5)	7216(4)	−4178(3)	3.4
C(30)	−8758(6)	8236(5)	−4655(4)	4.7
C(31)	−6594(6)	6796(6)	−4879(4)	4.8
C(32)	−7932(7)	6241(6)	−3600(4)	5.2
C(33)	−8081(7)	9829(6)	−2365(4)	5.2
C(34)	−8800(12)	9056(8)	−1785(6)	10.7
C(35)	−7380(10)	10429(13)	−1969(8)	14.9
C(36)	−9339(10)	10732(8)	−2937(7)	10.2
C(37)	−3257(5)	8832(4)	−3609(3)	2.9
C(38)	−3289(6)	9995(5)	−3438(4)	4.4
C(39)	−3062(5)	9045(5)	−4550(3)	3.6
C(40)	−1948(5)	7890(4)	−3078(3)	3.2

The germaoxaphosphorinene ring conformation is typically a sofa form with atoms OGePC(1) exactly planar (torsion angle O–Ge–P–C(1): 0°) and the six-membered ring folded along the O–C(1) axis: C(1)–C(2)–C(3)–O 4°, Ge–P–C(1)–C(2) 46°, P–Ge–O–C(3) −51°. In relation to the mean plane Ge–P–C(1)–C(2)–C(3)–O, O and C(1) are above this plane (respectively +0.45 and +0.44 Å), whereas Ge, P, C(2), and C(3) are below (respectively −0.15, −0.16, −0.32, and −0.27 Å).

The four atoms C(5)–Ge–P–C(23) also lie in a plane (torsion angle 0°). The angle between the two mesityl planes is 91°. The benzene ring of the Ar group is not planar but is deformed toward a boat form because of the large *tert*-butyl groups. Similar and even greater distortions of the Ar ring have been reported.[16]

The Ar group and the methyl bonded to the carbon C(1) are trans (torsion angle C(23)–P–C(1)C(4): −79°).

The sum of the angles at phosphorus (323.2°) is greater than generally observed for P(III) derivatives, for example, 297.8° in a tetraphosphinoethene[17] where phosphorus is

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substituted by a phenyl and two carbons, 307–309° in tetraphosphinoallene[18] where phosphorus is substituted by two phenyls and a carbon, and even lower in $P(SiH_3)_3$ (291°).[11] This slight flattening of the phosphorus pyramid accounts for the easy inversion at phosphorus.

Experimental Section

Since solutions of germaphosphenes 1 and 2 are highly air- and moisture-sensitive, their synthesis and handling require high-vacuum line techniques and carefully deoxygenated solvents (usually Et_2O, THF, pentane) which must be freshly distilled over sodium benzophenone.

^{1}H NMR spectra were recorded on Bruker AC 80, AC 200, and AC 250 instruments, respectively, at 80.1, 200.1, and 250.1 MHz. ^{13}C NMR spectra were recorded on Bruker AC 200 and AC 250 instruments, respectively, at 50.3 and 62.9 MHz (referenced to TMS). ^{31}P NMR spectra were recorded on a Bruker AC 80 instrument at 32.3 MHz (referenced to H_3PO_4 85%). IR spectra were recorded on a Perkin-Elmer 1600 FT instrument. Mass spectra were measured on a Hewlett Packard 5989A spectrometer by EI at 70 eV. Melting points were determined on a Reichert apparatus. Elemental analyses were performed by the "Service de microanalyse de l'Ecole de Chimie de Toulouse" (Toulouse, France).

General Procedures for Reaction of 1 with α-Ethylene Aldehydes and Ketones. Germaphosphene 1 was prepared as previously described[3c] by addition of 1 equiv of lithium phosphide $IsPLi_2$ to dimesityldifluorogermane Mes_2GeF_2 (1 g, 2.85 mmol) in Et_2O (20 mL). A solution of aldehyde or ketone (10% excess) in Et_2O was added directly to solutions of 1 without further purification. The reaction mixture changed from orange to light yellow. After 1 h of stirring at room temperature, Et_2O was removed in vacuo, 20 mL of pentane was added, and then LiF was filtered off. A ^{31}P NMR spectrum showed the formation of four- or six-membered ring derivatives and open-chain products with characteristic chemical shifts, in good yields (about 70% from Mes_2GeF_2). Cooling at -20 °C allowed the recrystallization of 3a and 9c; other compounds could not be recrystallized in completely pure form but were characterized by their NMR data.

3a: white crystals; mp 143–146 °C dec. ^{1}H NMR ($CDCl_3$), δ: 1.04 and 1.28 (2d, $^{3}J_{HH}$ 6.6 Hz, 2 × 6H, *o*-CH*Me* and *o*-CH*Me'*), 1.12 (d, $^{3}J_{HH}$ 6.9 Hz, 6H, *p*-CH*Me*$_2$), 1.99 and 2.06 (2s, 2 × 3H, *p*-Me), 2.37 and 2.76 (2s, 2 × 6H, *o*-Me), 2.55 (ddd, $^{2}J_{HH}$ 14.4 Hz, $^{3}J_{HH}$ 7.9 Hz, $^{3}J_{HP}$ 2.1 Hz, 1H, C*H*$_a$H$_b$P, *H cis/Is*), 2.68 (sept, $^{3}J_{HH}$ 6.9 Hz, 1 H, *p*-C*H*Me$_2$), 3.56 (ddd, $^{2}J_{HH}$ 14.4 Hz, $^{3}J_{HH}$ 5.1 Hz, $^{4}J_{HH}$ 2.1 Hz, 1H, CH$_a$*H*$_b$P, *H trans/Is*), 4.21 (sept, $^{3}J_{HH}$ 6.6 Hz, 2H, *o*-C*H*MeMe'), 4.86 (dddd, $^{3}J_{HC=CH}$ 5.5 Hz, $^{3}J_{HHb}$ 5.1 Hz, $^{3}J_{HHa}$ 7.9 Hz, $^{3}J_{HP}$ 8.0 Hz, 1H, OCH=C*H*), 6.50 and 6.70 (2s, 2 × 2H, arom H Mes), 6.65 (ddd, $^{3}J_{HH}$ 5.5 Hz, $^{4}J_{HHb}$ 2.1 Hz, $^{4}J_{HP}$ 3.4 Hz, 1H, OCH), 7.09 (d, $^{4}J_{HP}$ 2.4 Hz, 2H, arom H *Is*). ^{13}C NMR ($CDCl_3$), δ: 20.16 (d, $^{1}J_{CP}$ 23.5 Hz, CH$_2$P), 20.95 (*p*-Me), 24.57, 24.78, 25.86 and 26.10 (*o*-CH*Me*, *o*-CH*Me'*, *p*-CH*Me*$_2$ and *o*-Me), 33.50 (d, $^{3}J_{CP}$ 18.8 Hz, *o*-*C*HMeMe'), 34.48 (*p*-*C*HMe$_2$), 103.73 (OC=*C*H), 122.37 (*m*-C Is), 129.65 and 129.84 (*m*-C Mes), 137.45 and 137.58 (*p*-C Mes), 143.07 and 143.70 (*o*-C Mes), 148.57 (d, $^{2}J_{CP}$ 11.0 Hz, OC), 150.49 (*p*-C Is), 156.65 (d, $^{2}J_{CP}$ 14.6 Hz, *o*-C Is). MS (EI, 70 eV, ^{74}Ge), *m/z* (ion, relative intensity): 602 (M, 10), 546 (Mes$_2$Ge=PIs, 4), 483 (M – Mes, 1), 426 (MesGe=PIs – 1, 9), 367 (M – IsP – 1, 8), 329 (Mes$_2$Ge=O + 1, 39), 313 (Mes$_2$Ge + 1, 49), 311 (Mes$_2$Ge – 1, 57), 192 (MesGe – 1, 100). Anal. Calcd for $C_{36}H_{49}OPGe$: C, 71.90; H, 8.21. Found: C, 72.17; H, 8.40.

4a. ^{13}C NMR ($CDCl_3$), δ: 19.01–24.48 (C*Me*, *o*-CH*Me*, *o*-CH*Me'*, *p*-CH*Me*$_2$, *o*- and *p*-Me), 26.25 (d, $^{1}J_{CP}$ 18.6 Hz, CH$_2$P), 33.12–34.57 (*o*-*C*HMeMe' and *p*-*C*HMe$_2$), 114.33 (d, $^{2}J_{CP}$ 3.1 Hz, *C*=CO), 121.94 (d, $^{3}J_{CP}$ 3.1 Hz, *m*-C Is), 126.80 (d, $^{1}J_{CP}$ 48.2 Hz, ipso-C Is), 129.17 and 129.23 (*m*-C Mes), 138.60 and 138.85 (*p*-C Mes), 142.85 and 143.66 (*o*-C Mes), 149.96 (*p*-C Is), 153.07 (CO), 156.25 (d, $^{2}J_{CP}$ 14.7, *o*-C Is).

5a. ^{1}H NMR ($CDCl_3$), δ: 1.03–1.35 (m, 18H, *o*-CH*Me*, *o*-CH*Me'*, and *p*-CH*Me*$_2$), 2.18 (s, 3H, *p*-Me), 2.22 (s, 6H, *o*-Me), 2.26 (s, 3H, *p*-Me), 2.36 (d, $^{3}J_{HP}$ 1.4 Hz, 3H, *Me*CHP), 2.56 (s, 6H, *o*-Me), 2.82 (sept, $^{3}J_{HH}$ 7.0 Hz, 1H, *p*-C*H*Me$_2$), 3.59–3.80 (m, 3H, PCH and *o*-C*H*MeMe'), 4.59 (ddd, $^{3}J_{HC=CH}$ 5.7 Hz, $^{3}J_{HCCH}$ 3.9 Hz, $^{3}J_{HP}$ 7.4 Hz, 1H, C*H*=CHO), 6.44 (ddd, $^{3}J_{HC=CH}$ 5.7 Hz, $^{4}J_{HH}$ 2.4 Hz, $^{4}J_{HP}$ 4.0 Hz, 1H, CH=C*H*O), 6.69 and 6.78 (2s, 2 × 2H, H arom Mes), 6.93 (broad s, 2H, H arom Is). ^{13}C NMR ($CDCl_3$), δ: 20.55 (d, $^{1}J_{CP}$ 21.5 Hz, H(Me)*C*P), 20.99 (*p*-Me), 23.07 (d, $^{2}J_{CP}$ 2.8 Hz, H(*Me*)CP), 23.50, 23.79, 23.84, 24.23, 24.58, 24.73, 24.80 and 25.89 (*o*-Me, *o*-CH*Me*, *o*-CH*Me'*, and *p*-CH*Me*$_2$), 31.32 (broad s, *o*-*C*HMeMe'), 34.06 (*p*-*C*HMe$_2$), 111.71 (d, $^{3}J_{CP}$ 7.6 Hz, OCH=*C*H), 122.14 (broad s, *m*-C Is), 129.17 (*m*-C Mes), 138.65 and 138.86 (*p*-C Mes), 142.73 and 143.46 (*o*-C Mes), 142.90 (*p*-C Is), 146.67 (d, $^{3}J_{CP}$ 11.2 Hz, OCH), 150.27 (d, $^{4}J_{CP}$ 1.1 Hz, *o*-C Is). MS (EI, 70 eV, ^{74}Ge), *m/z* (ion, relative intensity): 616 (M, 14), 546 (Mes$_2$Ge=PIs, 45), 503 (Mes$_2$Ge=PIs – iPr, 5), 426 (Mes Ge=PIs – 1, 47) 313 (Mes$_2$Ge + 1, 29), 311 (Mes$_2$Ge – 1, 38), 303 (M – IsP – 1, 8), 233 (IsP – 1, 8), 192 (MesGe – 1, 100).

7a. ^{1}H NMR ($CDCl_3$), δ: 0.80 (d, $^{3}J_{HH}$ 6.6 Hz, *p*-CH*Me*$_2$), 1.18 and 1.22 (2d, $^{3}J_{HH}$ 6.8 Hz, 2 × 6H, *o*-CH*Me* and *o*-CH*Me'*), 1.64 (d, $^{4}J_{CP}$ 4.7 Hz, 3H, OC*Me*), 2.19 and 2.23 (2s, 2 × 3H, *p*-Me), 2.22 and 2.61 (2s, 2 × 6H, *o*-Me), 2.82 (sept, $^{3}J_{HH}$ 6.6 Hz, 1H, *p*-C*H*Me$_2$), 3.36 (m, 1H, C*H*$_c$H$_d$P), 3.42 (m, 1H, CH$_c$*H*$_d$P), 3.93 (sept, $^{3}J_{HH}$ 6.8 Hz, 2H, *o*-C*H*MeMe'), 4.74 (m, 1H, *o*-C-C*H*), 6.66 and 6.78 (2s, 2 × 2H, arom H, Mes), 6.91 (d, $^{4}J_{HP}$ 2.4 Hz, arom H, Is). ^{13}C NMR ($CDCl_3$), δ: 20.95 (d, $^{1}J_{CP}$ 22.8 Hz, CH$_2$P), 20.98 (*p*-Me), 22.89, 22.92, 23.31, 23.78, 23.85, 24.32, 24.54, 24.69, 25.63 (*o*-CH*Me*, *o*-CH*Me'*, and *p*-CH*Me*$_2$, *o*-Me, OC*Me*), 33.26 (d, $^{3}J_{CP}$ 18.5 Hz, *o*-*C*HMeMe'), 34.07 (*p*-*C*HMe$_2$), 99.32 (d, $^{2}J_{CP}$ 3.7 Hz, OC=*C*H), 121.89 (d, $^{3}J_{CP}$ 3.6 Hz, *m*-C Is), 126.61 (d, $^{1}J_{CP}$ 48.1 Hz, ipso-C *Is*), 129.08 and 129.12 (*m*-C Mes), 138.56 and 138.77 (*p*-C Mes), 142.78 and 143.69 (*o*-C Mes), 149.88 (*p*-C Is), 156.16 (d, $^{2}J_{CP}$ 14.4 Hz, *o*-C Is), 156.73 (d, $^{3}J_{CP}$ 11.6 Hz, OCH).

8a. ^{13}C NMR ($CDCl_3$), δ: 13.75–26.10 (*Me*C=C*Me*, *o*-CH*Me*, *o*-CH*Me'* and *p*-CH*Me*$_2$, *o*- and *p*-Me), 28.85 (d, $^{1}J_{CP}$ 24.9 Hz, CH$_2$P), 33.26, 33.63 and 34.15 (*o*-*C*HMeMe' and *p*-*C*HMe$_2$), 110.04 (d, $^{2}J_{CP}$ 3.4 Hz, PCH$_2$*C*), 121.78 (*m*-C Is), 127.43 (d, $^{1}J_{CP}$ 51.6 Hz, ipso-C Is), 129.07 and 129.23 (*m*-C Mes), 138.37 and 138.66 (*p*-C Mes), 142.71 and 143.89 (*o*-C Mes), 149.75 (*p*-C Is), 149.77 (d, $^{3}J_{CP}$ 12.1 Hz, CO), 156.18 (d, $^{2}J_{CP}$ 14.7 Hz, *o*-C Is). MS (EI, 70 eV, ^{74}Ge), *m/z* (ion, relative intensity): 630 (M, 11), 546 (Mes$_2$Ge=PIs, 32), 426 (MesGe=PIs – 1, 47), 395 (M – IsP + 1, 21), 329 (Mes$_2$Ge=O + 1, 32), 317 (M – Mes$_2$Ge – 1, 46), 313 (Mes$_2$Ge + 1, 43), 235 (IsP + 1, 32), 192 (MesGe – 1, 100).

9c: white crystals; mp 108–113 °C dec. ^{1}H NMR ($CDCl_3$), δ: 0.95 and 0.98 (2d, $^{3}J_{HH}$ 6.7 Hz, 2 × 6H, *o*-CH*Me* and *o*-CH*Me'*), 1.21 (d, $^{3}J_{HH}$ 6.8 Hz, 6H, *p*-CH*Me*$_2$), 2.04, 2.10 and 2.19 (3s, 3 × 6H, *o*- and *p*-Me), 2.82 (sept, $^{3}J_{HH}$ 6.8 Hz, 1H, *p*-C*H*Me$_2$), 3.35 (sept d, $^{3}J_{HH}$ 6.7 Hz, $^{4}J_{HP}$ 3.4 Hz, 2H, *o*-C*H*MeMe'), 5.57 (broad s, 1H, OC–C*H*), 6.66 (s, 4H, arom H, *Mes*), 6.84 (d, $^{4}J_{HP}$ 2.3 Hz, 2H, arom H, *Is*). ^{13}C NMR ($CDCl_3$), δ: 19.79 (=C*Me*, *Me trans/H*), 20.99 (*p*-Me), 23.32, 23.37, 23.46, 24.05 and 24.13 (*o*-CH*Me*, *o*-CH*Me'*, and *p*-CH*Me*$_2$), 26.61 (=C*Me*), *Me cis/H*), 33.21 (d, $^{3}J_{CP}$ 12.2 Hz, *o*-*C*HMeMe'), 34.42 (*p*-*C*HMe$_2$), 92.09 (=*C*H$_2$), 120.70 (d, $^{3}J_{CP}$ 3.2 Hz, *m*-C Is), 124.0 (d, $^{1}J_{CP}$ 25.5 Hz, ipso-C Is), 124.50 (OC=*C*H), 128.92 (*m*-C Mes), 135.81 (=*C*Me$_2$), 138.60 and 138.70 (*p*-C Mes), 142.69 and 142.77 (*o*-C Mes), 149.10 (*p*-C Is), 153.47 (d, $^{2}J_{CP}$ 9.1 Hz, *o*-C Is). MS (EI, 70 eV, ^{74}Ge), *m/z* (ion, relative intensity): 644 (M, 2), 601 (M – *i*Pr, 1), 546 (Mes$_2$Ge=PIs, 19), 503 (Mes$_2$Ge=PIs – *i*Pr, 3), 426 (MesGe=PIs – 1, 39), 409 (M – P(H)Is, 41), 329 (Mes$_2$GeO + 1, 20), 313 (Mes$_2$Ge + 1, 51), 203 (Is, 10), 193 (MesGe, 46), 98 (OC(=CH$_2$)CH=CMe$_2$ + 1, 47), 83 (OC(=CH$_2$)CH=CMe + 1, 100).

General Procedure for Reactions of 2 with α-Ethylene Aldehydes and Ketones. To an orange solution of germaphosphene 2 (between 0.92 and 1.10 g in all experiments) in pentane (10 mL) was added, at room temperature, a solution of aldehyde or ketone (10% excess) in the same solvent (5 mL). The orange solution turned rapidly light yellow; the reaction mixture was stirred for 1 h after the end of the addition. A ^{31}P NMR study showed the formation, depending on the aldehyde and

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[18] Schmidbaur, H.; Pollok, Th.; Reber, G.; Muller, G. *Chem. Ber.* 1987, *120*, 1403.

ketone used, of four-membered ring, six-membered ring, or open-chain products which were easily and unambiguously identified by their characteristic chemical shifts. The yields of adducts calculated by NMR are in all cases nearly quantitative. Recrystallization of crude material from pentane at −20 °C allowed the isolation of pure crystalline **3a′** and **5a′**; the other adducts were obtained in the form of powders having traces of impurities. However, NMR data proved their identity unambiguously.

3a′: white crystals; mp 155–158 °C dec. ^{1}H NMR (CDCl$_3$), δ: 1.28 (s, 9H, *p*-tBu), 1.40 (s, 18H, *o*-tBu), 2.13 (s, 12H, *o*-Me), 2.19 (s, 6H, *p*-Me), 3.19 (dt, $^{2}J_{HP}$ 6.3 Hz, $^{3}J_{HH}$ 6.3 Hz, $^{4}J_{HH}$ 1.3 Hz, 2H, CH$_2$P), 4.85 (ddt, $^{3}J_{CH-CH}$ 6.3 Hz, $^{3}J_{CH=CH}$ 5.8 Hz, $^{3}J_{HP}$ 10.6 Hz, 1H, OCH=C*H*), 6.42 (ddt, $^{3}J_{CH=CH}$ 5.8 Hz, $^{4}J_{HH}$ 1.3 Hz, $^{4}J_{HP}$ 2.7 Hz, OC*H*), 6.66 (s, arom H, Mes), 7.16 (d, $^{4}J_{HP}$ 2.1 Hz, arom H, Ar). ^{13}C NMR (CDCl$_3$), δ: 20.96 (*p*-Me), 23.69 (d, $^{1}J_{CP}$ 33.7 Hz, CH$_2$P), 24.20 (d, $^{4}J_{CP}$ 4.5 Hz, *o*-Me), 31.22 (*p*-C*Me*$_3$), 34.06 (d, $^{4}J_{CP}$ 6.4 Hz, *o*-C*Me*$_3$), 34.57 (*p*-*C*Me$_3$), 39.55 (d, $^{3}J_{CP}$ 3.6 Hz, *o*-*C*Me$_3$), 102.31 (d, $^{2}J_{CP}$ 4.6 Hz, OC=*C*H), 121.68 (d, $^{3}J_{CP}$ 7.0 Hz, *m*-C Ar), 127.80 (d, $^{1}J_{CP}$ 67.9 Hz, ipso-C *Ar*), 129.00 (*m*-C *Mes*), 138.10 (d, $^{2}J_{CP}$ 5.0 Hz, ipso-C Mes), 138.60 (*p*-C Mes), 143.13 (*o*-C), 147.82 (d, $^{3}J_{CP}$ 10.5 Hz, O*C*), 149.42 (d, $^{4}J_{CP}$ 2.3 Hz, *p*-C Ar), 159.48 (d, $^{2}J_{CP}$ 13.3 Hz, *o*-C Ar). MS (EI, 70 eV, ^{74}Ge), *m/z* (ion, relative intensity): 644 (M, 1), 587 (Mes$_2$Ge=PAr − 1, 95), 531 (Mes$_2$Ge=PAr − tBu, 2), 468 (MesGe=PAr − 1, 2) 411 (MesGe=PAr − tBu − 1, 1), 313 (Mes$_2$Ge + 1, 68), 277 (ArP + 1, 31), 220 (ArP − tBu + 1, 30), 192 (MesGe − 1, 100). Anal. Calcd for C$_{39}$H$_{55}$GeOP: C, 72.80; H, 8.62. Found: C, 72.81; H, 8.77.

4a′ (75%), 4b′ (25%). ^{13}C NMR (CDCl$_3$), δ: 19.49–24.37 (*Me*C, *o*- and *p*-Me), 30.19 ($^{1}J_{CP}$ 36.8 Hz, *C*H$_2$P **4a′**), 31.29–34.47 (*o*- and *p*-C*Me*$_3$), 34.66 and 34.99 (*p*-*C*Me$_3$), 38.52 (*o*-*C*Me$_3$ **4b′**), 39.59 (d, $^{3}J_{CP}$ 4.0 Hz, *o*-*C*Me$_3$ **4a′**), 92.12 (d, $^{1}J_{CP}$ 22.6 Hz, HCP **4b′**), 114.52 (d, $^{2}J_{CP}$ 4.0 Hz, *C*=CO **4a′**), 121.53–122.74 (*m*-C Ar), 127.25 (d, $^{1}J_{CP}$ 69.1 Hz, ipso-C Ar **4a′**), 129.07, 129.25 and 129.71 (*m*-C Mes), 138.00–149.55 (*o*- and *p*-C Mes and Ar), 159.82 (d, $^{2}J_{CP}$ 14.0 Hz, *o*-C Ar **4a′**).

5a′: white crystals; mp 162–165 °C dec. ^{1}H NMR (CDCl$_3$, 75 °C), δ: 1.20 (dd, $^{3}J_{HH}$ 7.0 Hz, $^{3}J_{HP}$ 10.5 Hz, 3H, *Me*CH), 1.24 (s, 9H, *p*-tBu), 1.47 (s, 18 H, *o*-tBu), 2.13 and 2.18 (2s, 2 × 3 H, *o*-Me), 2.56 (s, 12H, *p*-Me) 3.68 (m, 1H, C*H*Me), 4.54 (dt, $^{3}J_{HC=CH}$ 5.4 Hz, $^{3}J_{HC-CH}$ 4.1 Hz, $^{3}J_{HP}$ 5.4 Hz, 1H, OCH=C*H*), 6.28 (dt, $^{3}J_{HH}$ 5.4 Hz, $^{4}J_{HH}$ 2.6 Hz, $^{4}J_{HP}$ 2.6 Hz, 1H, OC*H*), 6.59 and 6.73 (2s, 2 × 2H, arom H Mes), 7.17 (d, $^{4}J_{HP}$ 2.0 Hz, 2H, arom H, *Ar*). ^{13}C NMR (CDCl$_3$), δ: 21.18 (*p*-Me), 21.78 (d, $^{1}J_{CP}$ 25.2 Hz, *C*HMeP), 23.55 (*o*-Me), 26.12 (d, $^{2}J_{CP}$ 13.8 Hz, *Me*CP), 31.38 (*p*-C*Me*$_3$), 34.27 (broad s, *o*-C*Me*$_3$), 34.69 (*p*-*C*Me$_3$), 38.96 (broad s, *o*-*C*Me$_3$), 115.30 (d, $^{2}J_{CP}$ 4.6 Hz, OC=*C*H), 121.81 (broad s, *m*-C, Ar), 129.39 (d, $^{1}J_{CP}$ 44.4 Hz, ipso-C Ar), 129.56 (*m*-C Mes), 136.95 (d, $^{2}J_{CP}$ 8.8 Hz, ipso-C Mes), 138.31 and 138.75 (*p*-C Mes), 138.85 (d, $^{2}J_{CP}$ 21.4 Hz, ipso-C Mes), 143.74 (*o*-C Mes), 147.60 (d, $^{3}J_{CP}$ 6.7 Hz, O*C*H), 149.69 (d, $^{3}J_{CP}$ 2.3 Hz, *p*-C Ar). Some signals are broad because of the coalescence phenomenon due to phosphorus inversion; moreover, the signal corresponding to the *o-C* of the Ar group could not be observed. MS (EI, 70 eV, ^{74}Ge), *m/z* (ion, relative intensity): 658 (M, 1), 588 (Mes$_2$Ge=PAr, 5), 531 (Mes$_2$Ge=PAr − tBu, 2), 468 MesGe=PAr − 1,3), 313 (Mes$_2$Ge + 1, 60), 275 (ArP − 1, 20), 192 (MesGe − 1, 100), 119 (Mes, 24), 70 (MeCH—CH=CHO, 96). Anal. Calcd for C$_{40}$H$_{57}$GeOP: C, 73.08; H, 8.74. Found: C, 72.88; H, 8.85.

6b′. ^{13}C NMR (CDCl$_3$), δ: 18.97 (Me trans/H, =C*Me*), 21.10, 22.88, 23.52 and 23.66 (*o*- and *p*-Me), 26.18 (Me cis/H, =C*Me*), 31.44 (*p*-C*Me*$_3$), 33.55 (d, $^{4}J_{CP}$ 7.6 Hz, *o*-C*Me*$_3$), 33.63 (*p*-*C*Me$_3$), 38.84 (*o*-*C*Me$_3$), 83.62 (d, $^{1}J_{CP}$ 15.0 Hz, OCH), 122.38 (*m*-C Ar), 128.09 (d, $^{2}J_{CP}$ 24.2 Hz, OCH—*C*H), 128.87 and 128.97 (*m*-C Mes), 130.84 (d, $^{1}J_{CP}$ 74.6 Hz, ipso-C Ar), 132.51 (d, $^{3}J_{CP}$ 14.2 Hz, *C*Me$_2$), 138.98 and 139.28 (*p*-C Mes), 142.51 and 143.71 (*o*-C Mes), 148.58 (*p*-C Ar), 154.12 (d, $^{2}J_{CP}$ 6.4 Hz, *o*-C Ar). MS (EI, 70 eV, ^{74}Ge), *m/z* (ion, relative intensity): 657 (M − 15, 1), 588 (Mes$_2$Ge=PAr, 18), 547 (Mes$_2$Ge(O)PAr − tBu, 29), 531 (Mes$_2$Ge=PAr − tBu, 10), 468 (MesGe=PAr + 1, 6), 397 (M − ArP + 1, 10), 329 (Mes$_2$Ge=O + 1, 100), 313 (Mes$_2$Ge + 1, 54), 192 (MesGe − 1, 58).

8a′. ^{1}H NMR (CDCl$_3$), δ: 1.24 (s, 9H, *p*-tBu), 1.40 (s, 18H, *o*-tBu), 2.15 (s, 6H, *p*-Me), 6.58 (broad s, 4H, arom Mes), 7.02 (d, $^{4}J_{HP}$ 1.8 Hz, 2H, arom Ar). Signals of Mes are broad due to hindered rotation. ^{13}C NMR (CDCl$_3$), δ: 18.36 and 19.01 (*Me*C=C*Me*), 20.90 (*p*-Me), 22.86 and 24.35 (*o*-Me), 31.42 (*p*-C*Me*$_3$), 32.55 (d, $^{1}J_{CP}$ 36.5 Hz, CH$_2$P), 34.38 (d, $^{4}J_{CP}$ 5.8 Hz, *o*-C*Me*$_3$), 39.30 (d, $^{3}J_{CP}$ 3.9 Hz, *o*-*C*Me$_3$), 109.72 (d, $^{2}J_{CP}$ 3.5 Hz, *C*=CO), 121.22 (d, $^{3}J_{CP}$ 6.8 Hz, *m*-C Ar), 126.56 (d, $^{1}J_{CP}$ 67.9 Hz, ipso-C Ar), 128.88 (broad s, *m*-C Mes), 138.06 (*p*-C Mes), 143.18 (broad s, *o*-C Mes), 149.16 (*p*-C Ar), 150.37 (d, $^{3}J_{CP}$ 10.4 Hz, CO), 159.51 (d, $^{2}J_{CP}$ 13.9 Hz, *o*-C Ar). MS (EI, 70 eV, ^{74}Ge), *m/z* (ion, relative intensity): 672 (M, 4), 615 (M − 57, 12), 588 (Mes$_2$Ge=PAr, 23), 531 (Mes$_2$Ge=PAr − 57, 6), 468 (MesGe=PAr + 1, 12), 395 (M − ArP − 1, 10), 359 (M − Mes$_2$Ge − 1, 20), 313 (Mes$_2$Ge + 1, 100), 192 (MesGe − 1, 71).

X-ray Structure Determination. Single crystals of **5a′** were obtained by cooling a solution of **5a′** in pentane to −20 °C for 2–3 days. Data were collected on a Huber diffractometer. Accurate cell dimensions were obtained from the centering of 18 reflections ($7 < 2\theta < 35°$). A standard reflection measured every 50 reflections showed no significant variation. The coordinates of the germanium atom were obtained by the interpretation of the Patterson function. The least-squares refinement was performed by SHELX 76 (C, P, O, Ge anisotropic). The hydrogens bonded to C(1), C(2), and C(3) were revealed by Fourier difference; other hydrogens were in calculated positions.

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Supplementary Material Available: Tables of complete bond lengths and angles, torsion angles, angles between planes, and anisotropic thermal parameters (4 pages). Ordering information is given on any current masthead page.

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