# The Reactivity of Phosphagermaallene Mes\*P=C=Ge(*t*-Bu)Tip toward Aldehydes and Ketones: an Experimental and Theoretical Study

F. Ouhsaine,<sup>†,‡</sup> E. André,<sup>§</sup> J. M. Sotiropoulos,<sup>§</sup> J. Escudié,<sup>\*,†</sup> H. Ranaivonjatovo,<sup>†</sup> H. Gornitzka,<sup> $\parallel$ </sup> N. Saffon,<sup> $\perp$ </sup> K. Miqueu,<sup>§</sup> and M. Lazraq<sup>‡</sup>

<sup>†</sup>Université de Toulouse, UPS, LHFA, 118 route de Narbonne, F-31062 Toulouse, France CNRS, LHFA, UMR 5069, F-31062 Toulouse cedex 09, France, <sup>‡</sup>Laboratoire d'Ingénierie Moléculaire et Organométallique (LIMOM), BP 1796, Faculté des Sciences Dhar El Mehraz, Université Sidi Mohamed Abdellah, Fès-Atlas, Fès, Morocco, <sup>§</sup>Institut Pluridisciplinaire de Recherche sur l'Environnement et les Matériaux, UMR-CNRS 5254, Université de Pau et des Pays de l'Adour, Hélioparc 2 Avenue du Président Angot, 64053 Pau cedex 09, France, <sup>II</sup>Laboratoire de Chimie de Coordination du CNRS, 205 route de Narbonne, 31077 Toulouse cedex 04, France, and <sup>⊥</sup>Structure Fédérative Toulousaine en Chimie Moléculaire, FR 2599, Université Paul Sabatier, 118 route de Narbonne, 31062 Toulouse cedex 09, France

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Phosphagermaallene Mes\*P=C=Ge(*t*-Bu)Tip 1 (Tip = 2,4,6-triisopropylphenyl, Mes\* = 2,4,6-tri-*tert*-butylphenyl) has been obtained by an improved synthesis in relation to the previously reported preparation starting from *t*-BuGeCl<sub>3</sub>. Very short Ge=C (1.761(2) Å) and P=C (1.625(2) Å) double bond lengths, trigonal planar geometry around the Ge atom, and GeCP bond angle of 166.57° are indicative of an heteroallenic structure for 1. Its reactions with crotonaldehyde and cinnamaldehyde lead to 1-oxa-2-germacyclobutanes by a [2 + 2] cycloaddition between the Ge=C and C=O double bonds; with methyl vinyl ketone, both a [2 + 4] cycloaddition between the Ge=C and the O=C-C=C moieties and an ene-reaction are observed leading to a 1-oxa-2-germacyclohex-5-ene and a germyl-(butadienyl)ether, respectively. With acetophenone, an ene-reaction occurs to afford exclusively a germyl(vinyl)ether. DFT calculations have been performed to explain the regiochemistry observed.

## Introduction

Heteroalkenes  $> E_{14}=C < (E_{14} = Si, {}^{1} Ge, {}^{1f,2} Sn^{1f,2b-d})$ , compounds in which one doubly bonded carbon atom has been replaced by a heavier element of group 14, have attracted much attention the last decades due to their great reactivity and their marked difference with the corresponding alkenes; their chemical behavior begins to be well-known. Meanwhile, the next challenge has been the synthesis of

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heteroallenes  $E_{14}=C=E'$ ,<sup>3</sup> compounds with an additional C=E' double bond to the  $E_{14}=C$  double bond; until now, only compounds of the type  $> E_{14}=C=C < (E_{14} = Si,^{4-6} Ge^{4,7})$  and  $> E_{14}=C=E_{15} - (E_{14} = Si, E_{15} = N,^{8} P,^{9} E_{14} = Ge, E_{15} = P;^{10} E_{14} = Sn, E_{15} = N^{11})$  have been obtained, and their chemical behavior is still poorly documented [SiCN

ORGANOMETALLICS

<sup>\*</sup>To whom correspondence should be addressed. Phone: (33) 5 61 55 83 47. Fax: (33) 5 61 55 82 04. E-mail: escudie@chimie.ups-tlse.fr.

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derivatives are better considered as silylene–isocyanide complexes than azasilaallenes > Si=C=N-; due to the easy cleavage of the silicon–carbon bond, they generally behave like silylenes and isocyanides; the same phenomenon has been reported for SnCN compounds]. We have prepared the first stable compound with two heavier group 14 and 15 elements, the phosphagermaallene Mes\*P=C=Ge(*t*-Bu)Tip (Tip = 2,4,6-triisopropylphenyl, Mes\* = 2,4,6-tri-*tert*-butylphenyl),<sup>10b</sup> and studied its chemical behavior toward chalcogens<sup>12</sup> and saturated aldehydes (benzaldehyde) and ketones (benzophenone, fluorenone).<sup>10b</sup> With such carbonyl derivatives, only [2 + 2] cycloadditions between the Ge=C and C=O double bonds leading to oxagermetanes have been observed (Scheme 1).

We have been interested in continuing our investigation on the chemical behavior of phosphagermaallene Mes\*P=C= Ge(t-Bu)Tip 1 by studying its reactivity with other types of carbonyl derivatives.

We present in this paper the reactivity of 1 toward  $\alpha$ -ethylenic aldehydes and ketones and toward a saturated ketone, which has protons in  $\alpha$  of the CO group, such as acetophenone. DFT calculations were used to explain the regiochemistry observed. In the first part, we describe an improved synthesis of phosphagermaallene 1, its X-ray structure, the first one for a heteroallene with two heavier doubly bonded group 14 and 15 elements, and its electronic configuration.

### **Results and Discussion**

a. Synthesis and X-ray Structure Determination of Phosphagermaallene Mes\*P=C=Ge(*t*-Bu)Tip 1. *tert*-Butyl-2,4,6-triisopropylphenyl(dimethoxy)germane 2 involved in the preparation of phosphagermaallene 1 was previously obtained from TipGeCl<sub>3</sub>, a derivative rather long to prepare in a pure state.<sup>10b</sup> The yield in dimethoxygermane Tip(*t*-Bu)Ge-(OMe)<sub>2</sub> 2 and its preparation time were improved starting from *t*-BuGeCl<sub>3</sub>,<sup>13</sup> followed by methoxylation to *t*-BuGe-(OMe)<sub>3</sub><sup>14</sup> and addition of TipLi. Phosphagermaallene 1 was then prepared as previously described in a quantitative yield according to <sup>31</sup>P NMR analysis by dechlorofluorination of the fluorophosphagermapropene 3 by *t*-BuLi at low temperature (Scheme 2).<sup>10b</sup>

Good single crystals of the extremely air and moisture sensitive phosphagermaallene 1 were obtained by cooling a saturated solution in  $\text{Et}_2\text{O}$  in a sealed tube; single crystals of 3 were obtained from pentane. Crystal structures of

#### Scheme 2



phosphagermapropene **3** and of phosphagermaallene **1** are presented in Figures 1 and 2.

In 3, torsion angles C21–P1–C1-Ge1  $(-164.94(9)^{\circ})$  and C21–P1–C1-Cl1  $(2.478(14)^{\circ})$  prove the formation of the *E*-isomer, as previously postulated.<sup>10b</sup> The three Ge–C bond lengths lie within the standard values,<sup>15</sup> as well as the P=C one.

The Ge=C double bond length in 1 (1.761(2) Å) is the shortest one reported until now; such a bond length is 1.783(2) Å in the germaallene Tbt(Mes)Ge=C= $CR_2^{7c}$  ( $CR_2$ = fluorenylidene, Tbt = 2,4,6-[(Me<sub>3</sub>Si)<sub>2</sub>CH]<sub>3</sub>C<sub>6</sub>H<sub>2</sub>) and generally between 1.77 and 1.86 Å in germenes > Ge=C  $< .^{16,17}$  A rather important shortening (10.2%) is observed in relation to the corresponding Ge1-C1 single bond (1.961(2) Å) in 3. The P=C bond length (1.625(2) Å) is in very good agreement with those reported in phosphaallene Mes\*P=C=CPh<sub>2</sub>  $(1.625(4)^{18a})$ and 1.63 Å<sup>18b</sup>) and in diphosphaallene Mes\*P=C=PMes\*  $(1.630(8) \text{ and } 1.635(8) \text{ } \text{Å}^{19})$ . The sum of angles on the germanium atom (359.77°) shows a planar environment around this atom. The angle  $\gamma$  between the mean plane C1–Ge1–C2– C6 and the plane C1-P1-C21 (84.0°) is close to the ideal 90° expected in a pure allenic structure and in good agreement with the corresponding angle reported for other heteroallenes (for example 79.3° in arsaallene Mes\*As=C=CR<sub>2</sub>, which has also doubly bonded group 14 and 15 elements).<sup>20</sup> The P1-C1-Ge1 bond angle (166.57(14)°) is also in the range of E=C=E' bond angles reported for other heteroallenes which generally vary from 159 to 175°: 159.2° in Tbt- $(Mes)Ge=C=CR_2$ ,<sup>7c</sup> 168.0° in Mes\*P=C=CPh<sub>2</sub>,<sup>18a</sup> 172.6(5)° in Mes\*P=C=PMes\*,<sup>19</sup> and 175.6(6)° in Mes\*As=C= AsMes\*.<sup>21</sup>

All these data (short Ge=C and P=C bond lengths, planarity around the Ge atom, wide P=C=Ge bond angle not far to  $180^{\circ}$ , and angle between planes C-Ge-C and C-P-C (84°) close to 90°) prove that **1** has an heteroallenic structure.

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**Figure 1.** Structure of **3**. Thermal ellipsoids are drawn at the 50% probability level. All hydrogen atoms are omitted for clarity. Selected bond lengths (Å), bond angles (deg) and torsion angles (deg): Ge1–F1 1.768(1), Ge1–C1 1.961(2), Ge1–C6 1.968(2), Ge1–C2 1.976(2), Cl1–C1 1.742(2), P1–C1 1.673(2), P1–C21 1.839(2), F1–Ge1–C1 96.23(6), F1–Ge1–C6 106.26(6), C1–Ge1–C6 114.09(7), F1–Ge1–C2 103.63(6), C1–Ge1–C2 116.53(6), C6–Ge1–C2 116.57(7), C1–P1–C21 102.96(8), P1–C1–C11 125.71(10), P1–C1–Ge1 119.22(9), C11–C1–Ge1 114.00(8), C11–C1–Ge1–F1–81.69(9), C21–P1–C1–Ge1 –164.94(9), C21–P1–C1–C11 2.478(14).



Figure 2. Structure of 1. Thermal ellipsoids are drawn at the 50% probability level. All hydrogen atoms and rotation disorder of *tert*-butyl group are omitted for clarity. Selected bond lengths (Å) and bond angles (deg): Ge1-C1 1.761(2), Ge1-C6 1.951(2), Ge1-C2 1.986(8), P1-C1 1.625(2), P1-C21 1.869(2), C1-Ge1-C6 114.43(9), C1-Ge1-C2 125.51(15), C6-Ge1-C2 119.81(15), C1-P1-C21 103.15(11), P1-C1-Ge1 166.57(14), angle between the mean plane C1-Ge1-C2-C6 and the plane C1-P1-C21 84.0.

b. Electronic Structure of Mes\*P=C=Ge(*t*-Bu)Tip 1 and HP=C=GeH<sub>2</sub> 1H. To go further into the description of the electronic structure of 1 and to study its possible chemical behavior with  $\alpha$ -ethylenic aldehydes and ketones (experimentally used), DFT calculations were carried out at the B3LYP/6-31G(d,p) level. The main geometrical parameters calculated for Mes\*P=C=Ge(*t*-Bu)Tip and the parent compound HP=C=GeH<sub>2</sub> 1H are reported in Table 1 and compared to the experimental ones.

One can notice a good agreement between calculated and experimental values, with variations of only  $\sim 0.01$  Å on bond lengths and of  $\sim 1.4\%$  on Ge–C–P bond angle. In particular, the planarity around the Ge atom and the orientation of the Mes\* group (R1) are well described. The main molecular orbitals (MO) of 1 and 1H have been drawn in Figure 3.

The frontier molecular orbitals (FMO) of **1** are centered on the allene fragment and contain almost no participation from Ge and P substituents. The LUMO corresponds to the  $\pi^*_{PC}$ orbital, while the HOMO can be described as an antibonding combination of the  $\pi_{GeC}$  orbital and the phosphorus lone pair  $n_p$ . These FMO are surrounded by the  $\pi^*_{GeC}$  orbital in LUMO+1, two  $\pi$  orbitals centered on the Mes\* group in HOMO-1 ( $\pi^1_{Mes*}$ ) and HOMO-2 ( $\pi^2_{Mes*}$ ), and the  $\pi_{PC}$  orbital in HOMO-3. It is noteworthy that the  $\pi_{GeC}$  orbital is more accessible than the  $\pi_{PC}$  one by about 1.25 eV. Thus, it appears that the reactivity involving the allene  $\pi$  system should occur preferentially on the Ge=C double bond.

The investigation of the geometrical parameters and the main molecular orbitals of the real molecule 1 gave meaningful information on the allene reactivity. However, in the case of mechanistic studies (particularly when looking for transition state structures), working with the complete system seems unreasonable in regard to computation time. The model compound 1H has been chosen, where sterically hindered substituents of Mes\*P=C=Ge(t-Bu)Tip have been replaced by hydrogen atoms. This approximation is motivated by the fact that the orbitals of the different substituents do not contribute significally to the FMO of 1. The main geometrical parameters of 1 and 1H are compared in Table 1. It appears that the results obtained for the experimental molecule and its model are in good agreement, showing that the replacement of sterically hindering substituents in 1 has a negligible effect on the phosphagermaallene geometry. The main MOs of 1H are depicted in Figure 3 and compared to those of 1. MOs in the 1H model are not modified to any great extent. One can note that the HOMO-3 in 1 corresponds to the HOMO-1 in 1H due to the absence of the two nonbonding  $\pi$  orbitals (HOMO-1 and HOMO-2) centered on the Mes\* group. The comparison of the MOs energetic positions in 1 and 1H reveals a global orbital energy shift for the model. This shift can be explained by the  $\sigma$ -donor effect of alkyl and aryl groups in 1 that destabilizes the allene orbital and makes them more accessible than in 1H. Despite this difference in energy, the shape and the order of the main MOs of the experimental molecule and of the model are almost identical. This means that 1 and 1H will share the same chemical behavior.

c. Theoretical Approach of the Reaction of HP=C=GeH<sub>2</sub> 1H with Methyl Vinyl Ketone and Crotonaldehyde. As a first approach, the reactivity of phosphagermaallene with  $\alpha$ -ethylenic aldehydes and ketones can be considered by means of the molecular orbital theory. To that purpose, the main orbitals of 1H and those of methyl vinyl ketone and crotonaldehyde are presented in Figure 4. These  $\alpha$ -ethylenic carbonyls are the most simple as well as the most commonly used in synthesis. As the nature of the main MOs of these two carbonyls is identical, only those of methyl vinyl ketone have been reported. The energy levels of crotonaldehyde orbitals are given in parentheses. The comparison between HOMO1H-LUMOcarbonyl and HOMO-1carbonyl-LUMO+ 11H gaps is, in both cases, in favor of a nucleophilic attack of the phosphagermaallene on the  $\alpha$ -ethylenic carbonyl (respectively 4.52 eV versus 5.83 eV for methyl vinyl ketone and 4.41 eV versus 5.55 eV for the crotonaldehyde). The HOMO of 1H, centered on  $\pi_{GeC}$ , would interact with the LUMO of the  $\alpha$ -ethylenic carbonyl. This latter corresponds to the bonding combination of the  $\pi^*_{CC}$  and  $\pi^*_{CO}$  orbitals.

From the theoretical point of view, interaction between Ge=C and C=O moieties have been reported in the

$P = C = Ge^{R_2}$ $R_1$ $R_3$	1 (Calcd)	1H (Calcd)	1 (Expt)
Ge-C	1.767	1.772	1.761(2)
C-P	1.634	1.640	1.625(2)
Ge-C-P	164.26	163.79	166.57(14)
γ	84.34	83.71	83.52
ΣGe	359.98	356.52	359.77



Table 1. Comparison of Selected Bond Lengths (Å) and Bond Angles (deg) Calculated for 1 and 1H with Experimental Results

Figure 3. Plot (cutoff: 0.05), nature (main contribution), and energetic positions ( $\varepsilon_i$ : Kohn–Sham energies) of the main molecular orbitals (MOs) for compounds 1 and 1H.

literature.<sup>22</sup> In particular, Mosey and co-workers have investigated the [2 + 2] cycloaddition between formaldehyde and germene H<sub>2</sub>C=GeH<sub>2</sub> and found a concerted mechanism with a barrier around 17 kcal·mol<sup>-1</sup> (DFT and CASSCF studies). In the present work, we investigated mechanistic studies involving the phosphagermaallene HP=C=GeH<sub>2</sub> and  $\alpha$ -ethylenic aldehydes and ketones. The presence of an unsaturation in the carbonyl compounds O=C(R)–C(H)=C(H)R' enriches the reactivity of this system. Indeed, aside from a [2 + 2] cycloaddition between the germanium carbon double bond and the carbonyl group, a [2 + 4]

cycloaddition can be also envisaged. The choice between these two mechanisms should depend on the contribution of each atom  $C_{\alpha}$ ,  $C_{\beta}$ , and O in the lowest unoccupied molecular orbital of the methyl vinyl ketone or crotonaldehyde. In particular, if the carbonyl carbon  $C_{\alpha}$  contribution (orbital coefficient) is more important than the one of  $C_{\beta}$ , then a [2 + 2] cycloaddition should be observed, involving a Ge=C attack on the  $C_{\alpha}$ =O. This reaction is symmetrically permitted through a supra-antara approach. On the contrary, if the  $C_{\beta}$  contribution for the LUMO orbital is more important than that of  $C_{\alpha}$ , a [2 + 4] cycloaddition should occur through a supra-supra attack of Ge=C on C=C<sub> $\beta$ </sub>. For the methyl vinyl ketone and crotonaldehyde, we have found that the  $C_{\alpha}$ and  $C_{\beta}$  contributions are similar in the LUMO, making

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**Figure 4.** Plot (cutoff: 0.05), nature (main contribution), and energetic positions ( $\varepsilon_i$ : Kohn–Sham energies) of the principal molecular orbitals (MO) for compounds **1H** and methyl vinyl ketone. The energetic positions of crotonaldehyde orbitals are given in parentheses.

possible both mechanisms. Consequently, it seemed interesting to experimentally explore the competition between these two cycloaddition reactions.

d. Reaction of 1 with Crotonaldehyde, Cinnamaldehyde, Methyl Vinyl Ketone, and Acetophenone. By addition of one molar equivalent of E-cinnamaldehyde to a cooled solution of 1 in Et<sub>2</sub>O, a unique new compound was observed in  $^{31}P$ NMR (4 = 254.3 ppm, d,  ${}^{3}J_{PH}$  = 15.8 Hz), which was isolated in 80% yield. With E-crotonaldehyde, two compounds **5** ( $\delta^{31}$ P = 257.9 ppm,  ${}^{3}J_{PH}$  = 15.2 Hz) and **5**' ( $\delta^{31}$ P = 257.0 ppm,  ${}^{3}J_{PH} = 14.3$  Hz) were formed in the ratio 85/15; only the major product 5 could be purified by fractional crystallization in 69% yield. The low-field <sup>31</sup>P chemical shifts for 4 and 5 proved that the P=C double bond was still present and that only the Ge=C unsaturation has been involved in the reaction. Four-membered ring structures formed by a [2 + 2] cycloaddition between the Ge=C and C=O double bonds were evidenced by the examination of the OCH moiety in <sup>13</sup>C NMR (4:  $\delta$  = 88.91 ppm,  $J_{CP}$  = 21.8 Hz, 5:  $\delta = 89.85 \text{ ppm}, J_{CP} = 21.4 \text{ Hz})$  and in <sup>1</sup>H NMR (4:  $\delta = 4.89 \text{ ppm}, \text{dd}, {}^{3}J_{HH} = 4.6 \text{ Hz}, {}^{3}J_{HP} = 15.8 \text{ Hz}; 5: \delta = 4.97 \text{ ppm}, \text{dd}, {}^{3}J_{HH} = 7.6 \text{ Hz}, {}^{3}J_{HP} = 15.2 \text{ Hz})$  (Scheme 3). In the sixmembered rings which would be formed by [2 + 4] cycloadditions between the Ge=C and the O=C-C=C units, the corresponding signals should be at much lower field. Thus, only the [2 + 2] cycloaddition between the Ge=C double



bond and the C=O moiety occurred to lead to oxagermetanes with exocyclic P=C double bonds (Scheme 3), contrary to the case of germene Mes<sub>2</sub>Ge=CR<sub>2</sub>,<sup>23</sup> where a [2 + 4] cycloaddition is observed with  $\alpha$ -ethylenic aldehydes. The structures of 4 (Figure 5) and 5 (Figure 6) were unambiguously proved by an X-ray structure determination. The C=C double bond presents as expected the *E*-configuration as in the starting aldehyde. For the P=C double bond, an *E*-configuration (Mes\* *trans* in relation to the germanium atom) was also determined and the Tip group, bulkier than

<sup>(23)</sup> Lazraq, M.; Escudié, J.; Couret, C.; Satgé, J.; Soufiaoui, M. Organometallics 1992, 11, 555.



**Figure 5.** Structure of **4**. Thermal ellipsoids are drawn at the 50% probability level. All hydrogen atoms and disorder of an isopropyl group are omitted for clarity. Selected bond lengths (Å) and bond angles (deg): Ge1-O1 1.825(9), Ge1-C1 1.952(13), O1-C2 1.429(15), C1-C2 1.559(19), Ge1-C11 1.975(14), Ge1-C15 1.983(14), P2-C1 1.637(15), P2-C30 1.865(12), C2-C3 1.514(17), C3-C4 1.315(17), C4-C5 1.476(17), O1-Ge1-C1 76.1(5), C2-O1-Ge1 95.0(7), C1-P2-C30 105.8(7), C2-C1-P2 140.0(9), C2-C1-Ge1 86.1(8), P2-C1-Ge1 133.9(7), O1-C2-C3 115.7(10), O1-C2-C1 102.5(9), C3-C2-C1 114.6(12).



Figure 6. Structure of 5. Thermal ellipsoids are drawn at the 50% probability level. All hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and bond angles (deg): Ge1-O1 1.831(1), Ge1-C1 1.965(2), O1-C2 1.451(2), C1-C2 1.539(2), Ge1-C28 1.953(2), Ge1-C24 1.984(2), C1-P1 1.661(2), P1-C6 1.860(2), C2-C3 1.490(2), C3-C4 1.310(2), C4-C5 1.499(2), O1-Ge1-C1 75.09(5), Ge1-C1-C2 87.14(9), C1-C2-O1 101.49(11), C2-O1-Ge1 95.13(8), C2-C1-P1 138.95(11), P1-C1-Ge1 133.09(8), C1-P1-C6 104.49(7), C3-C2-C1 117.46(12).

*t*-Bu, is on the same side as the H atom of the OCH moiety). As the <sup>31</sup>P chemical shifts and the <sup>3</sup>J<sub>PH</sub> coupling constants are about the same in **5** and **5**', we suppose that both compounds present an *E*-configuration of the P=C double bond. We tentatively assign **5**' to the isomer of **5** with Tip and the CH=CHMe moiety on the same side, such a feature being disfavored in the case of cinnamaldehyde due to the bulkier CH=CHPh.

Despite the high steric hindrance in derivatives 4 and 5, the intracyclic Ge-C bond lengths (1.954 to 1.966 Å) are in the normal range<sup>15</sup> as well as P-C and P=C distances. The



Figure 7. Structure of 6. Thermal ellipsoids are drawn at the 50% probability level. All hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and bond angles (deg): Ge1–O1 1.822(2), Ge1–C1 1.959(3), C1–C2 1.519(4), C2–C3 1.508(4), C3–C4 1.316(4), O1–C4 1.375(3), C4–C5 1.503(4), Ge1–C6 1.976(3), Ge1–C10 1.986(3), P1–C1 1.664(3), P1–C25 1.867(3), O1–Ge1–C1 95.62(10), C1–P1–C25 106.45(13), C4–O1–Ge1 121.84(18), C2–C1–P1 128.4(2), C2–C1–Ge1 110.48(19), P1–C1–Ge1 119.37(14), C3–C2–C1 114.2(2), C4–C3–C2 127.6(3), C3–C4–O1 125.7(3).

Ge–O bonds (1.825 to 1.831 Å) are slightly elongated in relation to the standard one 1.75-1.83 Å.<sup>15</sup>

The four-membered ring in oxagermetane **4** is nearly planar  $(01-Ge1-C1-C2 = 3.93^\circ, Ge1-C1-C2-O1 = -4.94^\circ, C1-C2-O1-Ge1 = 5.31^\circ and C2-O1-Ge1-C1 = -4.28^\circ);$  similar, however slightly larger torsion angles (7.24 to 9.71°), are found in oxagermetane **5**. Higher folding angles from 8 to 23° are generally reported in other oxagermetanes.<sup>24</sup>

By contrast to crotonaldehyde and cinnamaldehyde, a completely different reaction occurred with methyl vinyl ketone, leading to the six-membered ring compound 6 and to the germyl(butadienyl)ether 7 (ratio 40/60) (Scheme 3). The cyclic compound 6 was obtained in a pure state in 38% yield by fractional crystallization of the reaction mixture (pentane); unfortunately, the germylether 7 could not be isolated completely pure but was contaminated with about 10% of 6 (20% yield in 7). The six-membered ring structure of 6 was proved in the <sup>31</sup>P NMR spectrum without decoupling of proton by a doublet of doublet ( $J_{\rm PH} = 14.0$  and 21.3 Hz) due to the coupling of phosphorus with the two unequivalent protons of the CH<sub>2</sub> moiety. In a fourmembered ring 1-oxa-2-germetane (analogous to 4 and 5), these two protons should not couple with the phosphorus atom. Moreover, in the <sup>1</sup>H NMR spectrum, these two protons show signals at relatively high field (2.27 and 2.48 ppm) versus around 4 ppm expected for vinylic protons. The structure of 6 was unambiguously proved by an X-ray study (Figure 7), which displays, like those of 4 and 5, an E-configuration for the Mes\*P=C moiety.

The structure of 7 was also evidenced from the <sup>1</sup>H and <sup>13</sup>C NMR spectra by the presence of the HH'C=CH-C=CHH' moiety. In the <sup>31</sup>P NMR spectrum without proton decoupling, a doublet was observed at 336.0 ppm ( $J_{PH} = 23.4$  Hz), indicative of the presence of a proton on the sp<sup>2</sup> carbon atom doubly bonded to the phosphorus atom.

As both [2+4] cycloaddition and ene-reaction (or reaction with the enolic form, see further) occurred in the case of an

<sup>(24)</sup> Lazraq, M.; Couret, C.; Escudié, J.; Satgé, J.; Dräger, M. Organometallics 1991, 10, 1771.





 $\alpha$ -ethylenic ketone, which possesses a CH<sub>3</sub> bonded to the CO group, it was interesting to compare with another ketone, which has also a CH<sub>3</sub> bonded to the CO function; we have chosen acetophenone, which presents only the possibility of a [2 + 2] cycloaddition and not both [2 + 2] and [2 + 4] ones like methyl vinyl ketone.

In this case, only the ene-reaction was observed, leading to the sole germyl(ethenyl)ether **8**, which was isolated in 85% yield (Scheme 4). The structure of **8** was proved by the presence of vinylic protons at 3.73 and 3.42 ppm in the <sup>1</sup>H NMR spectrum and by a doublet at low field (331.6 ppm,  $J_{\rm PH} = 23.9$  Hz) in the <sup>31</sup>P NMR spectrum.

It was not possible in germylethers 7 and 8 to assign the configuration around the P=C double bond from the size of the  ${}^{2}J_{PH}$  and  ${}^{1}J_{PC}$  coupling constants. In the closely related phosphagermapropene Mes\*P=C(H)GeMe<sub>3</sub>,<sup>25</sup> with the same Mes\*P=C(H)Ge skeleton,  ${}^{2}J_{P=CH}$  couplings of 23.5 and 26.4 Hz and  ${}^{1}J_{P=C}$  couplings of 56.0 and 67.4 Hz have been reported for Z- and E-isomers, respectively. The  ${}^{2}J_{PH}$  coupling constants found in 7 (23.4 Hz) and in 8 (23.9 Hz) should be in favor of a Z-configuration, but the  ${}^{1}J_{PC}$  couplings (87.6 Hz in 7 and 76.0 Hz in 8) are in favor of the E-isomer.

Thus, when there is not the possibility of a [2 + 4] cycloaddition, the ene-reaction is the sole reaction to occur. A similar behavior was observed between germene Mes<sub>2</sub>-Ge=CR<sub>2</sub> and acetone, leading exclusively to the transient germyl(vinyl)ether Mes<sub>2</sub>Ge(CHR<sub>2</sub>)-OC(Me)=CH<sub>2</sub>.<sup>24</sup> However, in this case, this derivative underwent the Lutsenko rearrangement to give the more stable germylketone Mes<sub>2</sub>-Ge(CHR<sub>2</sub>)-CH<sub>2</sub>COMe.<sup>24</sup> Derivative **8**, probably due to a greater steric hindrance on the germanium atom, did not undergo such a rearrangement and was perfectly stable.

e. Theoretical Aspects of the Reactions. Methyl Vinyl Ketone. To look further into the reactivity of 1H, we compared the energy profiles of the different possible reactions leading to the experimentally characterized products. In the case of methyl vinyl ketone reaction, four different mechanisms can be considered as the most likely to occur (Figure 8): [2 + 2] and [2 + 4] cycloadditions affording 9H and 6H, respectively, and enereaction with the keto form or reaction with the enol form of methyl vinyl ketone to give 7H.

Experimentally, a mixture of compounds **6** and **7** is observed, which highlights the competition between at least two different mechanisms. While the presence of oxagermine **6** indicates that one of them is a [2 + 4] cycloaddition, the germyl(butadienyl)ether **7** can be formed in two different manners depending on the tautomeric form adopted by the methyl vinyl ketone. To determine the most favored pathway and thus the reactive form of the keto—enol equilibrium, the energetic profiles of the ene-reaction and of the reaction with the enol form are compared in Figure 9.

From the enol form, compound **7H** is obtained through the  $T_e$  transition state via a concerted asynchronous attack of the oxygen atom of the hydroxyl group on the germanium with a proton transfer to the allenic carbon. The activation energy is  $10 \text{ kcal} \cdot \text{mol}^{-1}$ , and the final product lies  $50 \text{ kcal} \cdot \text{mol}^{-1}$  below the reactants. In agreement with the Hammond postulate, the corresponding transition state structure is close to those of the reactants. The O1–H7 bond length is close to that of the enol form (1.06 Å versus 0.97 Å), while the C5–H7 distance is still long (1.76 Å). The Ge6–O1 distance (2.08 Å) is relatively long compared to what is observed in **7H** (1.82 Å).

For the keto form, the pathway is also a one step reaction involving the  $T_k$  transition state. Compound **7H** is obtained via a concerted, also asynchronous, attack of oxygen of the carbonyl group on the germanium atom with a proton transfer occurring, this time, from the methyl group to the allenic carbon. The transition state lies 11 kcal·mol<sup>-1</sup> over the reactants energy, while the product lies  $32 \text{ kcal} \cdot \text{mol}^{-1}$ below. The C5-H7 distance (1.78 Å) is comparable with that found for T<sub>e</sub> with a Ge6–O1 distance (1.98 Å) shorter than in Te. Whereas this latter is almost formed, coherent with the fact that in Tk the germanium environment is slightly tetrahedral ( $\Sigma Ge = 354^\circ$ ), the C5–H7 bond is not formed. The C6-H7 bond (1.19 Å) is longer than in the ketone (1.09 Å) with an increasing bond length (about 10%) comparable to the one of the hydroxyl in the enol form.

In the two different pathways, the final product shows an important thermodynamic stabilization compared with reagents, characteristic of nonreversible processes. The energy barriers of these two reactions have almost the same magnitude (11 and 10 kcal·mol<sup>-1</sup> for the keto and enol forms, respectively). This means that the two reactions have the same kinetic, or in other words that the two tautomers have the same reactivity. Therefore, the path favored depends only on the keto-enol equilibrium which is, as expected, shifted to the keto form  $(18 \text{ kcal} \cdot \text{mol}^{-1} \text{ more stable than enol})$ in the gas phase). This equilibrium is known to be sensitive to solvent.<sup>26</sup> In particular, the enol form can be stabilized by hydrogen bonding, but as the reaction occurs in aprotic solvent, the system should not be affected strongly by this effect and the situation should be close to the calculated one in gas phase. The keto tautomer is then the favored isomer, and thus the reaction with the enol form can be neglected in regard to the ene-reaction.

The energetic profiles of [2 + 2] and [2 + 4] cycloadditions have also been calculated. They are depicted in Figure 10 as well as the previously described ene-reaction.

The [2+2] cycloaddition mechanism is a one step reaction leading to the formation of compound **9H** through  $T_{[2+2]}$ . The allene attack on the carbonyl function occurs via an intermediate approach between supra-supra and supraantara facial (C2−O1−Ge6−C5 dihedral ≈39°). The structure of the TS is peculiar. The P8=C5 bond length remains in the range of a double bond, the Ge6-C5 bond length increases (+0.12 Å) compared with 1H and the GeCP bond angle decreases drastically (-40°). The C2-C5 bond has not been formed (3.02 Å). The Ge–O1 distance (1.96 Å) and the almost planar environment of the germanium atom ( $\Sigma Ge =$ 357°) indicate that only a weak interaction between the oxygen atom and the germanium one exists. This geometrical modification can be highlighted considering the shape of the MOs. The HOMO corresponds to a lone pair localized on the C5 atom in antibonding interaction with the phosphorus lone pair, whereas the LUMO+1 is a  $\pi^*_{P=C}$  orbital

<sup>(25)</sup> Goede, S. J.; Bickelhaupt, F. Chem. Ber. 1991, 124, 2677.

<sup>(26)</sup> Rappoport, Z., Ed., *The Chemistry of Enols*; Wiley: Chichester, UK, 1990.



**Figure 8.** Summary of the different mechanisms considered for reaction of **1H** with methyl vinyl ketone. Like for phosphagermaallene, the names of these products have been labeled with "H" to figure replacement of sterically hindering substituents by hydrogen atoms. (a) Ene-reaction or reaction with enolic form.



**Figure 9.** Energy profiles ( $\Delta G$  in kcal·mol<sup>-1</sup>) of the reaction between **1H** and the keto or enol form of methyl vinyl ketone.

(See Supporting Information for the plot of the MOs). As a consequence, this TS can be viewed as a carbenoid form.

The [2 + 4] cycloaddition leads to the formation of compound **6H** through  $T_{[2+4]}^{27}$ . In this mechanism, the allene approach is clearly supra–supra facial (C4–O1–Ge6–C5 dihedral angle  $\approx -5^{\circ}$ ). However, the attack deviates

by about 30° in relation to a standard supra-supra facial approach. The geometrical parameters of the allene moiety are not modified to any great extent compared to those calculated for **1H** (GeCP bond angle:  $+1^{\circ}$ , Ge=C: +0.016 Å, P=C: -0.002 Å). The Ge-O1 and C4-C5 bonds have not yet been formed (2.22 and 3.15 Å, respectively) but the mechanism remains asynchronous.

Like the ene-reaction, both of the cycloadditions are exergonic, **6H** being the thermodynamic product of these

<sup>(27)</sup> A first step, consisting in a  $180^{\circ}$  rotation of the terminal CH<sub>2</sub> group around the C2-C3 axis, has been omitted for the sake of clarity.



**Figure 10.** Energy profiles ( $\Delta G$  in kcal·mol<sup>-1</sup>) of [2 + 2] and [2 + 4] cycloadditions as well as ene-reaction for methyl vinyl ketone. Selected bond lengths (Å) and bond angles (deg).

reactions. Indeed, **6H** is 24 kcal  $\cdot$  mol<sup>-1</sup> more stable than **9H**, and 18 kcal·mol<sup>-1</sup> more stable than **7H**. The comparison of the activation energies for the two cycloaddition reactions is also in favor of the [2+4] cycloaddition (8 kcal·mol<sup>-1</sup> versus 18 kcal·mol<sup>-1</sup> for the [2 + 2] one). Thus, it seems clear that the [2+4] cycloaddition is preferred to the [2+2] one. When the [2+4] cycloaddition is compared to the ene-reaction, one can note that both reactions present a barrier lower than that found for the [2 + 2] cycloaddition. The difference in energy between the two activation barriers (3 kcal·mol<sup>-1</sup>) is too small to differentiate the kinetics of the two mechanisms. This leads to the conclusion that the reactions occur simultaneously to form the two products. Computational considerations are in agreement with experimental results: a mixture of compound 6 and 7 is observed while compound 9 is not formed.

**Crotonaldehyde.** In the case of the reaction with crotonaldehyde, the [2+2] and [2+4] cycloadditions are also the reactions in competition. By contrast with methyl vinyl ketone, the [2+2] cyclo-product is the unique species obtained experimentally. The [2+2] and [2+4] cycloaddition pathways are presented in Figure 11. The geometrical parameters of the two transition states exhibit characteristics similar to those calculated for methyl vinyl ketone. The difference in energy between **5H** and **10H** is significant (15 kcal·mol<sup>-1</sup>) and in favor of the [2 + 4]cycloadduct, which is the most thermodynamically stable compound. However it is noteworthy that, for both pathways, the important stabilization of the products compared to the reactants prevents the reversibility of the processes.

The comparison of the two activation barriers is here slightly in favor of the [2 + 2] cycloaddition (13 kcal·mol<sup>-1</sup> versus 15 kcal·mol<sup>-1</sup> for [2 + 4] cycloaddition). The difference in energy is too small to be significant, but it stresses out a difference in behavior compared to the case of methyl vinyl

ketone. When going from the ketone to the aldehyde, the activation energy of the [2+2] cycloaddition is decreased by 5 kcal·mol<sup>-1</sup>, while the one of [2 + 4] cycloaddition is increased by 7 kcal·mol<sup>-1</sup>. The competition between the two mechanisms seems to be influenced by the carbonyl derivatives. Nevertheless, taking into account the small difference between the two activation barriers, it was difficult for us to conclude unambiguously. The steric hindrance of the phosphagermaallene could also affect the small difference in energy of the calculated activation barriers. For this reason, the [2 + 2] and [2 + 4] cycloaddition barriers have also been calculated with the real molecule 1. In this case, the approach of the carbonyl is hindered by the phosphagermaallene substituents, as shown by the activation barriers (18 kcal·  $mol^{-1}$  for [2 + 2] and 22 kcal·mol<sup>-1</sup> for [2 + 4] cycloaddition), which are slightly higher than with 1H. But, more important, the difference in energy between the two mechanisms, although still small, is slightly more marked. This confirms the trend observed with the model compound and tends to show that the [2 + 2] species observed experimentally with crotonaldehyde is the kinetically controlled product of the reaction while the [2 + 4] cycloadduct obtained with the ketone is the both kinetically and thermodynamically controlled derivative.

In conclusion, phosphagermaallene 1, which presents a typical heteroallenic structure, is very reactive toward  $\alpha$ -ethylenic aldehydes and ketones and acetophenone. In all cases, only the Ge=C double bond has been involved in the reactions. When ene-reactions and [2 + 2] cycloadditions are possible, the ene-reaction occurs exclusively (case of acetophenone). By contrast, when an ene-reaction is in competition with a [2 + 4] cycloaddition (case of methyl vinyl ketone), both reactions occur. DFT calculations show that the reaction with the enol form can be neglected in relation to the ene-reaction and allow to understand the regiochemistry of the reactions.



Figure 11. Reaction of 1H with crotonaldehyde. Energy profiles ( $\Delta G$  in kcal·mol<sup>-1</sup>) of [2 + 2] and [2 + 4] cycloadditions. Selected bond lengths (Å) and bond angles (deg).

## **Experimental Section**

All experiments were carried out in flame-dried glassware under an argon atmosphere using high-vacuum-line techniques. Solvents were freshly dried using an SPS-5MB system. NMR spectra were recorded (with CDCl<sub>3</sub> as solvent) on a Bruker Avance 300 spectrometer at the following frequencies: <sup>1</sup>H, 300.13 MHz (reference TMS); <sup>13</sup>C, 75.47 MHz (reference TMS); <sup>31</sup>P, (121.51 MHz) (reference H<sub>3</sub>PO<sub>4</sub>). Melting points were determined on a Wild Leitz-Biomed apparatus. Mass spectra were obtained on a Hewlett-Packard 5989A spectrometer by EI at 70 eV and on a Nermag R10-10 spectrometer by CI. Elemental analyses were performed by the "Service de Microanalyse de l'Ecole de Chimie de Toulouse"

tert-Butyl(trimethoxy)germane. t-BuGe(OMe)3 was obtained as previously described<sup>14</sup> from t-BuGeCl<sub>3</sub><sup>13</sup> and identified by its bp  $(117-119 \text{ °C}/10^{-2} \text{ mm Hg})$  and <sup>1</sup>H NMR spectrum.

 $^{3}$ C NMR  $\delta$  (ppm): 28.16 (CMe<sub>3</sub>), 31.10 (CMe<sub>3</sub>), 54.48 (OMe). MS (EI, 70 eV, m/z, %): 224 (M, 3), 192 (M – MeOH, 10), 168 (M - t-Bu + 1, 15), 137 (M - t-Bu - OMe + 1, 60), 105 (M *t*-Bu – 2OMe, 60), 57 (*t*-Bu, 100).

tert-Butyl-2,4,6-triisopropylphenyl(dimethoxy)germane. A solution of n-BuLi 1.6 M in hexane (19 mL, 30 mmol) was added to a solution of TipBr (8.5 g, 30 mmol) in 60 mL of THF cooled to -80 °C. After 2 h stirring, TipLi was slowly canulated to a solution of t-BuGe(OMe)<sub>3</sub> (6.7 g, 30 mmol) cooled to -80 °C. The reaction mixture was warmed to room temperature, solvents were eliminated in vacuo, and 30 mL of pentane were added. Pure  $Tip(t-Bu)Ge(OMe)_2$  was obtained from pentane as white crystals (9.61 g, 75%) and identified by NMR and mp to Tip(t-Bu)Ge(OMe)<sub>2</sub> previously obtained by the reaction between t-BuLi and TipGe(OMe)3.14

3-tert-Butyl-3-(2,4,6-triisopropylphenyl)-1-(2,4,6-tri-tert-butylphenyl)phosphagermaallene 1. Phosphagermaallene 1 was synthesized as previously described<sup>10b</sup> by addition of a solution of *tert*-butyllithium 1.6 M in pentane (1.1 mL) to a solution of fluorophosphagermapropene Mes\*P=C(Cl)-Ge(t-Bu)(F)Tip 3 (1.04 g,

1.54 mmol) in Et<sub>2</sub>O (20 mL) cooled to -78 °C. The reaction mixture became immediately red. By gradually warming to room temperature, a red-orange solution was obtained. A <sup>31</sup>P NMR analysis ( $\delta$ 249.9 ppm) showed the quantitative formation of phosphagermaallene 1. In all cases, addition of aldehydes and ketones was performed on such crude solutions of phosphagermaallene 1 containing LiF without further purification.

Reaction of Cinnamaldehyde with Phosphagermaallene 1. Cinnamaldehyde (180 mg, 1.36 mmol) was added via syringe to a solution of 1 (1.34 mmol) cooled to -50 °C; an orange coloration was observed. After stirring overnight, LiF was eliminated by filtration; 4 crystallized from Et<sub>2</sub>O by cooling at -20 °C; white crystals of 4 were washed with pentane: 805 mg (80%), mp 180 °C.

<sup>1</sup>H NMR  $\delta$  (ppm): 1.16 and 1.22 (2s, 2 × 9 H, *t*-BuGe and *p*-*t*-Bu of Mes\*), 1.19-1.31 (m, 18H, CHMeMe' of Tip), 1.42 and 1.47 (2s, 2 × 9H, o-t-Bu of Mes\*), 2.80-3.00 (m, 3H, CHMe-Me'of Tip), 4.89 (dd,  ${}^{3}J_{HP} = 15.8$  Hz,  ${}^{3}J_{HH} = 4.6$  Hz, 1H, O–CH), 5.36 (dd,  ${}^{3}J_{HH} = 4.6$  Hz,  ${}^{3}J_{HH} = 16.0$  Hz, 1H, CH-CH–O), 6.28 (d,  ${}^{3}J_{HH} = 16.0$  Hz, 1H, Ph–CH), 6.99 and 7.00 (2s, 2 × 1H, arom H of Tip), 7.08-7.22 (m, 5H, H of Ph), 7.27 and 7.31 (2s, 2 × 1H, arom H of Mes\*).

<sup>13</sup>C NMR δ (ppm): 23.58, 23.84, 23.97, 25.38, 27.09, 27.40 (d,  $J_{\rm PC} = 5.5$  Hz), 34.20 and 34.92 (CH and CH<sub>3</sub> of Tip), 27.83 and 31.33 (GeCMe<sub>3</sub> and p-CMe<sub>3</sub>), 32.96 (d,  $J_{PC} = 6.0$  Hz) and 33.72  $(d, J_{PC} = 8.3 \text{ Hz})$  (*o*-CMe<sub>3</sub>), 37.79 and 37.98 (CMe<sub>3</sub>), 88.91 (d,  $J_{CP} = 21.8$  Hz, OCH), 120.81, 121.13, 122.03, and 122.60 (arom CH of Mes\* and Tip), 126.61, 127.32, and 128.04 (arom CH of Ph and PhCH), 129.73 (d,  $J_{CP} = 7.8$  Hz, =CHCHO), 131.37 (d,  $J_{CP} = 5.3$  Hz, *ipso*-C of Tip), 137.70 (*ipso*-C of Ph), 138.63 (d,  $J_{CP} = 69.1$  Hz, *ipso-C* of Mes\*), 149.56, 150.51, 152.51, 153.03, 153.38, and 154.80 (arom C of Mes\*, Ph and Tip), 196.73  $(d, J_{CP} = 73.0 \text{ Hz}, C=P).$ 

<sup>31</sup>P NMR  $\delta$  (ppm): 254.3 (d, <sup>3</sup>J<sub>PH</sub> = 15.8 Hz). MS (EI, 70 eV, m/z, %): 754 (M<sup>+</sup>, 20), 738 (M<sup>+</sup> – O, 7), 698  $(M^+ - t-Bu + 1, 25), 641 (M^+ - 2t-Bu + 1, 80), 565 (M^+ - t-BuGe$ -t-Bu -1, 30), 509 (M<sup>+</sup> -t-BuGe -2t-Bu, 70), 493 (M<sup>+</sup> - Mes\*

1	3
C <sub>38</sub> H <sub>61</sub> GeP	C <sub>38</sub> H <sub>61</sub> ClFGeP
621.43	675.88
173(2)	173(2)
$0.40 \times 0.30 \times 0.05$	$0.40 \times 0.40  imes 0.40$
monoclinic	monoclinic
C2/c	C2/c
43.1008(7)	32.739(3)
10.2532(2)	10.024(1)
17.4178(3)	25.812(2)
90	90
98.543(1)	113.402(2)
90	90
7611.9(2)	7774.2(12)
8	8
0.869	0.926
53069	26637
9396 [R(int) = 0.0530]	11804 [R(int) = 0.0361]
semiempirical	semiemppirical
0.9579 and 0.7226	1.0000 and 0.7084
9396/132/413	11804/0/397
1.026	1.025
R1 = 0.0413, wR2 = 0.0926	R1 = 0.0376, wR2 = 0.0883
R1 = 0.0693, wR2 = 0.1032	R1 = 0.0622, wR2 = 0.0972
0.484 and -0.298	0.551 and -0.366
	$\frac{1}{C_{38}H_{61}GeP}$ $\frac{621.43}{173(2)}$ $0.40 \times 0.30 \times 0.05$ monoclinic $\frac{C2/c}{43.1008(7)}$ $10.2532(2)$ $17.4178(3)$ $90$ $98.543(1)$ $90$ $7611.9(2)$ $8$ $0.869$ $53069$ $9396 [R(int) = 0.0530]$ semiempirical $0.9579$ and 0.7226 $9396/132/413$ $1.026$ $R1 = 0.0413, wR2 = 0.0926$ $R1 = 0.0693, wR2 = 0.1032$ $0.484$ and -0.298

-0,35, 465 (M<sup>+</sup> – Mes\*P=C – 1, 15), 421 (M<sup>+</sup> – Mes\*P – t-Bu, 15), 403 ( $M^+$  – Tip(*t*-Bu)GeO – 1, 40), 275 (Mes\*P – 1, 60), 57 (t-Bu, 100).

Anal. Calcd for C<sub>47</sub>H<sub>69</sub>GeOP (754.43) C, 74.91; H, 9.23%. Found: C, 75.28; H, 9.36%.

Reaction of Crotonaldehyde with Phosphagermaallene 1. Crotonaldehyde (102 mg, 1.46 mmol) was added via syringe to a solution of phosphagermaallene 1 (1.46 mmol) cooled to -50 °C. An orange coloration appeared immediately. A <sup>31</sup>P NMR spectrum showed the formation of 2 products at 257.9 ppm ( ${}^{3}J_{PH} = 15.2 \text{ Hz}$ ) (85%) and 257.0 ppm ( ${}^{3}J_{PH} = 14.3 \text{ Hz}$ ) (15%). After elimination of LiF by filtration, the filtrate was crystallized from Et<sub>2</sub>O; only the major isomer 5 was isolated as white crystals (695 mg, 69%, mp 182 °C).

<sup>1</sup>H NMR  $\delta$  (ppm): 1.11 (d, <sup>3</sup>J<sub>HH</sub> = 6.6 Hz, 6H, *o*-CH*MeMe'* of Tip), 1.19 (d,  ${}^{3}J_{HH} = 6.9$  Hz, 6H, *o*-CH*MeMe'* of Tip), 1.28  $(d, {}^{3}J_{HH} = 6.2 \text{ Hz}, 6\text{H}, p\text{-CH}MeMe' \text{ of Tip}), 1.13 \text{ and } 1.24 (2s,$  $2 \times 9$ H, *t*-BuGe and *p*-*t*-Bu of Mes\*), 1.35 and 1.48 (2s,  $2 \times 9$ H, *o-t*-Bu of Mes\*), 1.39 (d,  ${}^{3}J_{\text{HH}} = 6.5$  Hz, 3H, MeCH=), 2.79 (sept,  ${}^{3}J_{HH} = 6.8 \text{ Hz}$ , 3H, CHMeMe' of Tip), 4.51 (dq,  ${}^{3}J_{HH} = 6.7 \text{ Hz}$ ,  ${}^{3}J_{HH} = 14.9 \text{ Hz}$ , 1H, CH=CHMe), 4.85 (ddd,  ${}^{4}J_{HP} = 1.5 \text{ Hz}$ ,  ${}^{3}J_{HH} = 7.6 \text{ Hz}$ ,  ${}^{3}J_{HH} = 14.9 \text{ Hz}$ , 1H, CH=CHMe), 4.97  $(dd, {}^{3}J_{HH} = 7.6 \text{ Hz}, {}^{3}J_{HP} = 15.2 \text{ Hz}, 1H, CHO), 6.93 (s, 2H,$ arom H of Tip), 7.15 and 7.23 (2s,  $2 \times 2H$ , arom H of Mes\*).

<sup>13</sup>C NMR  $\delta$  (ppm): 18.00 (*Me*CH), 23.43, 23.90 (d,  $J_{PC} = 8.4$ Hz), 25.47, 26.97, 27.42 (d,  $J_{PC} = 5.9$  Hz), 34.17, 34.80, and  $37.50 (d, J_{PC} = 5.8 Hz) (CH and CH<sub>3</sub> of Tip), 27.86 and 31.44$ (GeCMe<sub>3</sub> and p-CMe<sub>3</sub>), 32.87 (d,  $J_{PC} = 6.2$  Hz, o-CMe<sub>3</sub>) and 33.77 (d,  $J_{PC} = 8.3$  Hz, o-CM $e_3$ ), 34.87, 37.83, 37.93 (CM $e_3$ ), 89.85 (d,  $J_{PC} = 21.4$  Hz, OCH), 120.7, 121.06, 121.29, and 122.29 (arom CH of Tip and Mes\*), 123.93 (=CHMe), 131.40 (d,  ${}^{3}J_{CP} = 5.3$  Hz, *ipso*-C of Tip), 131.93 (d,  $J_{PC} = 7.9$  Hz, CH=CHMe), 137.62 (d,  ${}^{1}J_{PC} = 70.0$  Hz, *ipso*-C of Mes\*), 148.99, 150.43, 152.34 (d, J<sub>PC</sub>=2.8 Hz), 152.46, 153.31 and 154.82 (arom C of Tip and Mes\*), 197.24 (d,  $J_{PC} = 73.0$  Hz, C=P). <sup>31</sup>P NMR  $\delta$  (ppm): 257.9 (d,  ${}^{3}J_{PH} = 15.2$  Hz).

MS (EI, 70 eV, m/z, %): 692 (M<sup>+</sup>, 30), 635 (M<sup>+</sup> - *t*-Bu, 30), 579 (M<sup>+</sup> - 2*t*-Bu + 1, 100), 447 (M<sup>+</sup> - Mes\*, 50), 341 (M<sup>+</sup> -TipGeO - t-Bu - 1, 50), 289 (TipGeC, 50), 277 (TipGe, 90), 275 (Mes\*P - 1, 90), 231 (TipGe - iPr - 3, 40), 57 (t-Bu, 100).

Anal. Calcd for C<sub>42</sub>H<sub>67</sub>GeOP (691.55) C, 72.95; H, 9.77%. Found: C, 73.11; H, 9.66%.

Reaction of Methyl Vinyl Ketone with Phosphagermaallene 1. Methyl vinyl ketone (100 mg, 1.42 mmol) was added to a solution of phosphagermaallene (1.42 mmol) cooled to -50°C. After warming to room temperature, a <sup>31</sup>P NMR spectrum showed the formation of two derivatives at 277.0 and 336.1 ppm (ratio 40/60). The solvents were eliminated under reduced pressure and replaced by 30 mL of pentane. LiF was eliminated by filtration. By recrystallization from pentane, the oxagermine 6 was the first to crystallize and could be obtained completely pure (375 mg, 38%, mp 125 °C). By contrast, the germylether 7 could only be obtained in 90% purity with the presence of about 10% of **6**.

**Oxagermine 6.** <sup>1</sup>H NMR  $\delta$  (ppm): 1.14–1.20 (m, CH<sub>3</sub> of Tip), 1.26 and 1.27 (2s, 2 × 9H, t-BuGe and p-t-Bu of Mes\*), 1.39 and 1.47 (2s, 2 × 9H, o-t-Bu of Mes\*), 1.57 (s, 3H, Me); 2.27 (ddd,  ${}^{2}J_{\rm HH'} = 17.6 \text{ Hz}, {}^{3}J_{\rm HP} = 14 \text{ Hz}, {}^{3}J_{\rm HH'} = 6.4 \text{ Hz}, 1\text{H}, CHH'),$ 2.48 (ddd,  ${}^{2}J_{HH'} = 17.6 \text{ Hz}$ ,  ${}^{3}J_{HP} = 21.3 \text{ Hz}$ ,  ${}^{3}J_{HH'} = 2.0 \text{ Hz}$ , 1H, CHH'), 2.80 (sept,  ${}^{3}J_{HH} = 6.9$  Hz, 1H, *p*-CHMeMe' of Tip), 3.4 (broad s,  $\Delta v_{1/2} = 24.5$  Hz, 1H, *o*-CHMeMe' of Tip), 3.68 (dd,  ${}^{3}J_{HH'} = 6.4$  Hz,  ${}^{3}J_{HH'} = 2.0$  Hz, 1H, CHH'-CH), 3.78 (broad s,  $\Delta v_{1/2} = 25.9$  Hz, 1H, *o*-CHMeMe' of Tip), 6.98 (2s, 2 × 1H, arom H of Tip), 7.30 (2s, 2 × 1H, arom H of Mes\*). <sup>13</sup>C NMR δ (ppm): 22.03, 22.77 (d,  $J_{CP}$  = 3.5 Hz), 23.50

(broad s), 25.09 (broad s), 25.76 (broad s), 26.70 (broad s), 27.45  $(d, J_{PC} = 5.6 \text{ Hz}), 30.31, 30.83 \text{ (broad s)}, 32.36, 32.45, and 32.91$ (CH and CH<sub>3</sub> of Tip, GeCMe<sub>3</sub>, CMe<sub>3</sub> of Mes\* and Me), 29.31,  $33.54 (d, {}^{2}J_{PC} = 16.1 \text{ Hz}), 33.85, 37.00, \text{ and } 37.10 (d, J_{PC} = 1.0 \text{ Hz})$  $(CH_2 \text{ and } CMe_3)$ , 93.43 (d,  $J_{PC} = 6.4 \text{ Hz}$ , =CH), 120.05, 120.23 (broad s), 120.61, and 121.55 (broad s) (arom CH of Tip and Mes\*), 128.20 (d,  $J_{PC} = 8.9$  Hz, *ipso*-C of Tip), 135.32 (d,  $J_{PC} = 76.5$  Hz, *ipso*-C of Mes\*), 148.40, 148.54, 151.26, 153.26, 153.41 (d,  $J_{PC} = 2.9$ Hz), 153.55, 156.01 (arom C of Tip and of Mes\*, =CMe), 181.77 (d,

 $J_{CP} = 74.3 \text{ Hz}, C=P).$ <sup>31</sup>P NMR  $\delta$  (ppm): 273.13 (dd, <sup>3</sup> $J_{PH} = 14 \text{ Hz}, <sup>3</sup><math>J_{PH} = 21.3 \text{ Hz}).$ MS (EI, 70 eV, m/z, %): 692 (M<sup>+</sup>, 10), 635 (M<sup>+</sup> - *t*-Bu, 100), 579 (M<sup>+</sup> - 2 *t*-Bu +1, 10), 565 (M<sup>+</sup> - 2 *t*-Bu - CH<sub>3</sub> + 2, 5), 360 (Tip(t-Bu)GeO-C + 2, 70), 277 (Mes\*P + 1, 90), 57 (t-Bu, 100).

Anal. Calcd for C<sub>42</sub>H<sub>67</sub>GeOP (691.55) C, 72.95; H, 9.77%. Found: C, 72.81; H, 9.56%.

Germylether 7. <sup>1</sup>H NMR  $\delta$  (ppm): 0.62–1.70 (m, CH*MeMe'* of Tip and t-Bu), 2.69-2.86 (m, 3H, CHMeMe' of Tip), 3.70 (s, 1H, OC=CHH'), 3.92 (s, 1H, OC=CHH'), 5.01 (d,  ${}^{3}J_{HH} = 10.2$ Hz, 1H, CH=CHH'; H cis in relation to H), 5.67 (d,  ${}^{3}J_{HH'}$  = 16.9 Hz, 1H, CH=CHH'; H' trans in relation to H), 6.09 (ddd,  ${}^{4}J_{\rm HH} = 1$  Hz,  ${}^{3}J_{\rm HH} = 10.2$  Hz,  ${}^{3}J_{\rm HH'} = 16.9$  Hz, CH=CHH'),

Table 3. Crystal Data for Compounds	4,	, 5, and 6	,
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	4	5	6
empirical formula	C <sub>47</sub> H <sub>69</sub> GeOP	C <sub>42</sub> H <sub>67</sub> GeOP	C <sub>42</sub> H <sub>67</sub> GeOP
formula wt	753.58	691.52	691.52
temp (K)	173(2)	173(2)	173(2)
crystal size (mm <sup>3</sup> )	$0.60 \times 0.40 \times 0.40$	$0.60 \times 0.40 \times 0.40$	$0.20 \times 0.20 \times 0.10$
cryst syst	monoclinic	monoclinic	triclinic
space group	C2/c	$P2_1/n$	$P\overline{1}$
a (Å)	37.647(14)	10.239(1)	10.0287(4)
$b(\mathbf{A})$	9.876(4)	15.474(1)	14.7045(5)
$c(\dot{A})$	29.559(17)	25.510(2)	14.8994(6)
α (deg)	90	90	102.737(2)
$\beta$ (deg)	127.753(4)	92.992(1)	106.859(2)
$\gamma$ (deg)	90	90	98.330(2)
$V(Å^3)$	8689(7)	4036.4(4)	1999.02(13)
Z	8	4	2
abs coeff $(mm^{-1})$	0.774	0.827	0.835
no. of rflns collected	18893	49041	15929
no. of ind rflns	4473	9198	8110
	[R(int) = 0.1194]	[R(int) = 0.0307]	[R(int) = 0.0552]
abs cor	none	none	semiempirical
max/min transmission			0.9211 and 0.8508
no. of data/restraints/params	4473/85/495	9198/0/425	8110/0/425
goodness of fit on $F^2$	1.235	1.028	0.987
final R indices	R1 = 0.1250,	R1 = 0.0297,	R1 = 0.0463,
(I > 2s(I))	wR2 = 0.2576	wR2 = 0.0740	wR2 = 0.0879
R indices (all data)	R1 = 0.1528,	R1 = 0.0419,	R1 = 0.0835,
	wR2 = 0.2690	wR2 = 0.0813	wR2 = 0.1006
largest diff peak,	0.549	0.52	0.501
hole (e $A^{-3}$ )	and -0.988	and -0.220	and -0.566

7.78 (d,  ${}^{2}J_{\rm HP}$  = 23.4 Hz, 1H, CH=P), 6.91 (s, 2H, arom H of Tip), 7.27 (s, 2H, arom H of Mes\*).  ${}^{13}$ C NMR  $\delta$  (ppm): 22.74, 24.57, 25.15, 27.42 (d,  $J_{\rm CP}$  = 5.1

Hz), 30.28, 30.60, 32.55, 32.88, 33.00, 33.05, 33.15 (CH and CH<sub>3</sub> of Tip and CMe<sub>3</sub>), 28.70 and 37.08 (CMe<sub>3</sub>), 94.44 (OC=CH<sub>2</sub>), 112.41 (CH=CH<sub>2</sub>), 120.63, 120.68, and 121.16 (arom CH of Tip and Mes\*), 128.95 (d,  $J_{PC} = 7.0$  Hz, *ipso*-C of Tip), 135.50 (CH<sub>2</sub>=CH), 142.96 (d,  $J_{PC} = 73.1$  Hz, *ipso*-C of Mes\*), 148.21, 148.79, 149.58 (d,  $J_{CP} = 4.3$  Hz), 151.80, 154.18, and 155.98 (arom C of Tip and of Mes\*, CO), 169.71 (d,  $J_{PC} = 87.6$  Hz, P=CH).

<sup>31</sup>P NMR  $\delta$  (ppm): 336 (d, <sup>2</sup>J<sub>HP</sub> = 23.4 Hz).

MS (EI, 70 eV, m/z, %): 692 (M<sup>+</sup>, 20), 635 (M<sup>+</sup> - *t*-Bu, 70), 579 (M<sup>+</sup> - *t*-Bu + 1, 25), 447 (M<sup>+</sup> - Mes<sup>\*</sup>, 90), 415 (M<sup>+</sup> -Mes\*P - 1, 25), 57 (t-Bu, 100).

Reaction of Acetophenone with Phosphagermaallene. Acetophenone (169 mg, 1.41 mmol) was added to a solution of phosphagermaallene (1 equiv) cooled to -50 °C. The solution became red immediately. After stirring overnight at room temperature, the solvents were removed in vacuo and replaced by 30 mL of pentane. LiF was filtrated off; cooling the pentanic solution to -20 °C

afforded 889 mg (85%, mp 205 °C) of white crystals of **8**. <sup>1</sup>H NMR  $\delta$  (ppm): 0.93 (d, <sup>3</sup>J<sub>HH</sub> = 6.4 Hz, 6H, *o*-CH*MeMe'* of Tip), 1.09 (d, <sup>3</sup>J<sub>HH</sub> = 6.4 Hz, 6H, *o*-CH*MeMe'* of Tip), 1.14  $(d, {}^{3}J_{HH} = 6.9 \text{ Hz}, 6\text{H}, p\text{-CH}MeMe' \text{ of Tip}), 1.21 (s, 9\text{H}, p\text{-}t\text{-Bu})$ or t-BuGe), 1.27-1.33 (m, 27H, t-BuGe or p-t-Bu and o-t-Bu of Mes\*), 2.73 (sept,  ${}^{3}J_{HH} = 6.9$  Hz, 1H, *p*-CHMeMe' of Tip), 3.07 (broad s,  $\Delta v_{1/2} = 29.5$  Hz, 2H, *o*-CHMeMe' of Tip), 3.73 (s, 1H, C=CHH'), 4.42 (s, 1H, C=CHH'), 6.91 (s, 2H, arom H of Tip), 7.16–7.23 (m, 5H, arom H of Ph), 7.63 (m, 2H, arom H of Mes\*), 7.84 (d,  ${}^{2}J_{\text{HP}} = 23.9 \text{ Hz}$ , 1H, P=*CH*).

<sup>13</sup>C NMR  $\delta$  (ppm): 23.88, 25.76, 26.30, 28.63 (d,  $J_{PC} = 4.7$ Hz), 31.40, 33.76, and 34.09 (d,  $J_{PC} = 9.9$  Hz) (CMe<sub>3</sub>, CH and CH<sub>3</sub> of Tip), 29.64 and 34.87 (GeCMe<sub>3</sub> and *p*-CMe<sub>3</sub> of Mes\*), 38.19 (o-CMe<sub>3</sub> of Mes\*), 90.51 (C=CH<sub>2</sub>), 121.82 and 122.36 (arom CH of Mes\* and Tip), 125.68, 127.85, and 127.84 (arom CH of Ph), 129.95 (d,  $J_{PC} = 0.9$  Hz, *ipso*-C of Tip), 139.9 (*ipso*-C of Ph), 143.88 (d,  $J_{PC} = 73.2$  Hz, *ipso*-C of Mes\*), 149.36, 149.99, 152.93, 155.28, and 157.91 (arom C of Mes\* and Tip and CO), 170.86 (d,  $J_{PC} = 76.0$  Hz, C=P). <sup>31</sup>P NMR  $\delta$  (ppm): 331.65 (d,  ${}^{2}J_{PH} = 23.9$  Hz).

MS (EI, 70 eV, m/z, %): 742 (M<sup>+</sup>, 0.5), 685 (M<sup>+</sup> - *t*-Bu, 1),  $623 (M^+ - PhCOMe + 1, 1), 565 (M^+ - PhCOMe - t-Bu, 20),$  $465 (M^+ - Mes^*P - 1, 90), 57 (t-Bu, 100).$ 

Anal. Calcd for C<sub>46</sub>H<sub>69</sub>GeOP (741.61) C, 74.50; H, 9.38%. Found: C, 74.71; H, 9.46%.

X-ray Structure Determinations for 1, 3, 4, 5, and 6. All data were collected at low temperatures using an oil-coated shockcooled crystal on a Bruker-AXS APEX II diffractometer with Mo K $\alpha$  radiation ( $\lambda = 0.71073$  Å). The structures were solved by direct methods<sup>28</sup> and all non-hydrogen atoms were refined anisotropically using the least-squares method on  $F^2$  (Tables 2 and 3).<sup>29</sup>

In the case of compound 4, we obtained only weak diffracting crystals resulting in high R values; only the data with the resolution between 1 and 4 Å were taking into account for the refinement (Table 3).

Computational Details. Calculations were performed with the Gaussian 03 suite of programs,<sup>30</sup> using the density functional method.<sup>31</sup> The hybrid exchange functional B3LYP<sup>32</sup> set was used. B3LYP is a three parameter functional developed by Becke that combines the Becke gradient-corrected exchange

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functional and the Lee–Yang–Parr and Vosko–Wilk–Nusair correlation functional with part of the exact HF exchange energy. All Gaussian calculations were done in combination with the 6-31G(d,p) basis set for all atoms. Geometry optimizations were carried out without any symmetry restrictions; the nature of the extrema (minimum and transition states) was verified with analytical frequency calculations. To ensure that the transition states are connected to the right minima, IRC calculations were conducted using the Schlegel–Gonzalez algorithm.<sup>33</sup> All Gibbs free energies have been zero-point energy

(ZPE) and temperature corrected using unscaled density functional frequencies.

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**Supporting Information Available:** CIF files for **1**, **3**, **4**, **5**, and **6**. Theoretical calculation details. This material is available free of charge via the Internet at http://pubs.acs.org.

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