DOI: 10.1002/ejic.201000747

# Reactivity of Quinones with Phosphagermaallene Tip(*t*Bu)Ge=C=PMes* Leading to Four- and Six-Membered Heterocycles with an Exocyclic P=C Double Bond

**Dumitru Ghereg,[a] Heinz Gornitzka,[b] and Jean Escudié*[a]**

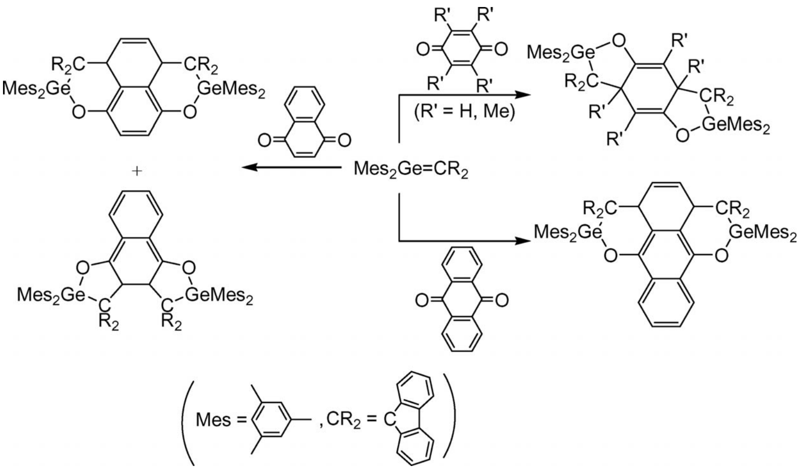
**Keywords:** Main group elements / Germanium / Phosphorus / Cumulenes / Quinones / Cycloaddition

Phosphagermaallene Tip(*t*Bu)Ge=C=PMes* (**1**) (Tip = 2,4,6-triisopropylphenyl, Mes* = 2,4,6-tri-*tert*-butylphenyl) reacts with one equivalent of *p*-quinone (1,4-benzoquinone, 2,3,5,6-tetramethyl-1,4-benzoquinone, 1,4-naphthoquinone, and 9,10-anthraquinone) to form spiro 1-oxa-2-germacyclobutane compounds **2**–**5** with an exocyclic P=C double bond by [2 + 2] cycloaddition between the Ge=C and one of the C=O double bonds. With two equivalents of **1** a double [2 + 2] cycloaddition occurs involving both unsaturated C=O bonds of 1,4-benzoquinone to give the dispiro compound **6**. [2 + 4] Cycloadditions are observed between the Ge=C double bond of **1** and the O=C–C=O unit of an α-diketone (benzil) and an *o*-quinone (9,10-phenanthrenequinone) to give the corresponding 1,4-dioxa-2-germa-5-cyclohexenes **7** and **8**.

## Introduction

Heteroalkenes $E^{14}$=C ($E^{14}$ = Si,[1] Ge,[2] Sn[2a,2d]) have been intensively studied over the last three decades. Owing to the great reactivity of the $E^{14}$=C double bond, these compounds are powerful building blocks in organometallic and heterocyclic chemistry. In the field of germanium unsaturated derivatives, the reactivity of germene $Mes_2Ge=CR_2$ (Mes = 2,4,6-trimethylphenyl, $CR_2$ = fluorenylidene) and, in some cases, of $Mes_2Ge=CR'_2$ ($CR'_2$ = 2,7-di-*tert*-butylfluorenylidene) towards quinones has been reported very recently. Depending on the quinone, a variety of reactions occur at the Ge=C double bond (Scheme 1).

For example, [2 + 4] cycloadditions involving the O=C–C=CH unit with naphthoquinone[3] and anthraquinone[4] and two different types of formal [2 + 3] cycloadditions involving the O=C–CH unit with naphthoquinone,[3] 1,4-benzoquinone,[5] and 2,3,5,6-tetramethyl-1,4-benzoquinone have been observed.[5] Whatever the stoichiometry of the reagents, the final product is formed from two molecules of germene and one of quinone.



Scheme 1. Reactivity of $Mes_2Ge=CR_2$ towards *p*-quinones.

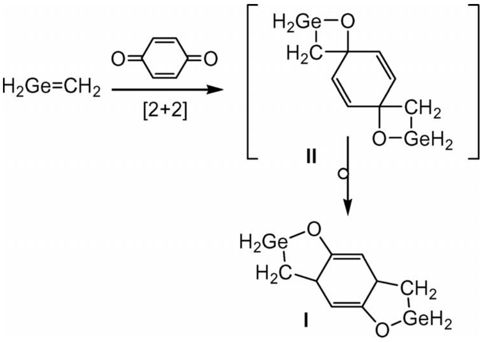
In order to understand the surprising reaction leading to the five-membered ring oxagermacyclopentanes, DFT calculations have been performed on 1,4-benzoquinone and the model compound $H_2Ge=CH_2$. They predict that the

---

[b] CNRS, LCC (Laboratoire de Chimie de Coordination),
Université de Toulouse, UPS, INP, LCC,
205 route de Narbonne, 31077 Toulouse, cedex 4, France
[a] Université de Toulouse, UPS, LHFA; CNRS, LHFA, UMR 5069,
118 route de Narbonne, 31062 Toulouse, cedex 09, France
E-mail: escudie@chimie.ups-tlse.fr

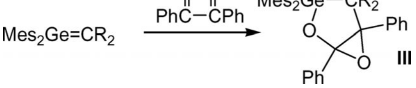
© 2011 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

first step of the reaction leading to **I** is a double [2 + 2] cycloaddition between the Ge=C and C=O double bonds to give transient dispiro compound **II**, with two four-membered oxagermacyclobutane rings, followed by its rearrangement to give the final adduct with five-membered rings (Scheme 2).[5]



Scheme 2. Postulated reaction of $H_2Ge=CH_2$ with 1,4-benzoquinone.

In the case of α-diketones such as benzil, a surprising reaction occurs leading to the formation of compound **III** according to an unexpected new type of epoxidation reaction[6] (Scheme 3).



Scheme 3. Reaction of $Mes_2Ge=CR_2$ with benzil.

Heteroallenes $E^{14}=C=E'$[7] ($E^{14}$ = Si, Ge; E′ = C,[8,9] N,[10] P[11]), particularly those with two heavy group 14 and 15 elements, are still relatively rare and their chemical behavior has been less explored.

After our studies on the reactivity of the germene $Mes_2Ge=CR_2$ towards quinones and α-diketones, we have been interested by a comparison with the reactivity of the phosphagermaallene Tip(*t*Bu)Ge=C=PMes*[11a] (**1**) towards the same quinones and α-diketones. This heteroallene is theoretically able to react through its Ge=C and/or P=C double bonds, and also by the lone pair on the phosphorus atom.

Thus, we present here the reactivity of **1** towards four *p*-quinones (1,4-benzoquinone, 2,3,5,6-tetramethyl-1,4-benzoquinone, 1,4-naphthoquinone, and 9,10-anthraquinone) and benzil. We also report the chemical behavior of **1** towards an *o*-quinone, phenanthrenequinone, which is structurally close to benzil.

## Results and Discussion

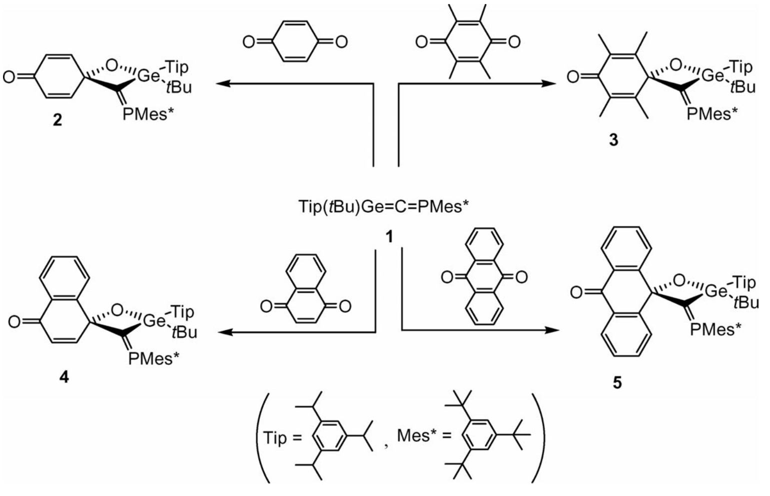
### *p*-Quinones

1,4-Benzoquinone, 2,3,5,6-tetramethyl-1,4-benzoquinone, 1,4-naphthoquinone, and 9,10-anthraquinone were added to solutions of **1** cooled to –80 °C in a 1:1 molar ratio. The $^{31}P$ NMR spectrum of the crude reaction mixture showed in all cases the formation of only one product. Low-field chemical shifts (328.2 to 336.3 ppm) indicated that the P=C double bonds were not involved in the reaction.[12] This is also confirmed by the low-field chemical shifts (185.76–195.36 ppm) in the $^{13}C$ NMR spectra with a large $^1J_{CP}$ (62.1 to 67.2 Hz) corresponding to the carbon atoms doubly bonded to phosphorus. Signals between 86.75 and 93.50 ppm ($^2J_{CP}$ from 32.7 to 41.6 Hz) correspond to an oxygen-bound carbon atom. Similar chemical shifts were observed in the 1-oxa-2-germacyclobutanes obtained from **1** and benzaldehyde, benzophenone, and fluorenone.[11a]

In the $^{13}C$ NMR spectra, the presence of signals between 185.12 and 186.84 ppm prove that one carbonyl group is still present and that the [2 + 2] cycloaddition between the Ge=C and C=O bonds occurred with only one C=O double bond.

All these data are in agreement with the formation of compounds **2**–**5** (Scheme 4).

The $^1H$ NMR spectra display only one doublet for the diastereotopic methyl groups of the *p*-*i*Pr of Tip due to their great distance to the chiral center and, as expected, two doublets for the methyl groups of the *o*-*i*Pr groups. The



Scheme 4. Reaction of **1** with *p*-quinones to form **2**–**5**.

© 2011 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

presence of only two doublets prove the free rotation of the Tip group around the Ge–C(*ipso*) bond. Two singlets are observed for the *o*-*t*Bu groups of Mes* due to its hindered rotation on the NMR time scale.

The structure of **3** was unambiguously confirmed by an X-ray study (Figure 1).

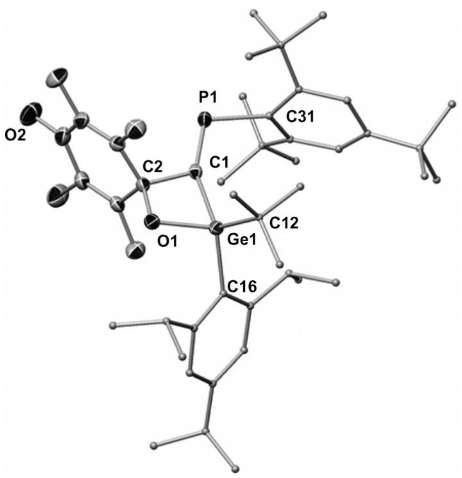


Figure 1. Structure of **3**. Thermal ellipsoids are drawn at the 50% probability level. All hydrogen atoms are omitted and Tip, *t*Bu, and Mes* have been simplified for clarity. Selected bond lengths [Å] and angles [°]: Ge1–C1 2.008(2), Ge1–C12 1.998(2), Ge1–C16 1.986(2), Ge1–O1 1.835(2), O1–C2 1.449(3), C1–C2 1.574(3), P1–C1 1.675(2), P1–C31 1.840(2), O1–Ge1–C1 73.9(1), C2–O1–Ge1 98.0(2), O1–C2–C1 99.8(2), C2–C1–Ge1 87.3(2).

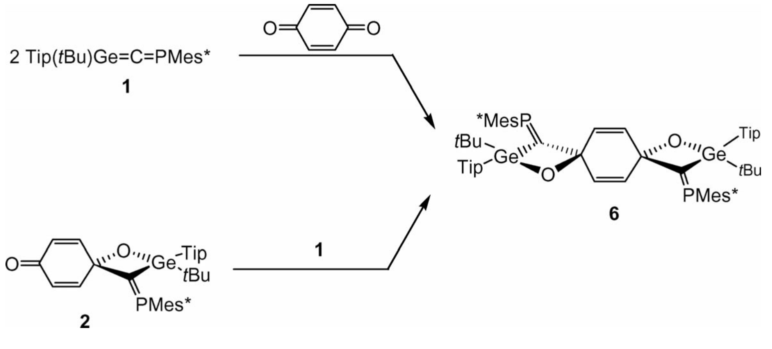
The Ge–C bond lengths [1.986(2) to 2.008(2) Å] are at the upper limit of the Ge–C bond-length range (1.94–1.98 Å)[13] similar to the Ge–O bond length of 1.835(2) Å (generally 1.73–1.78 Å).[13] The P=C double bond presents a *Z*-configuration (Mes* and Ge on the same side), and the four-membered ring is nearly planar (Ge1–O1–C2–C1 –8.59°, Ge1–C1–C2–O1 7.78°). Generally, 1-oxa-2-germacyclobutane rings are slightly more folded (for example 18.9°[11a] and 23°[14]). The geometry of the carbon atom of the C=P double bond is nearly planar (sum of angles: 358.1°).

The addition of two equivalents of **1** to 1,4-benzoquinone or of one equivalent of **1** to derivative **2** yielded a sole derivative, as proved by $^{31}$P NMR analysis of the crude reaction mixture. The product was identified as the double cycloadduct **6** (Scheme 5). This dispiro derivative was characterized by $^{1}$H, $^{13}$C, and $^{31}$P NMR spectra, which give similar data as for **2**, except for the absence of a C=O group, and thus the formation of a double cycloadduct is concluded. The formation of only one isomer could be due to the difference in size between the involved groups.

Thus, although only the Ge=C double bond is involved in the reaction, the chemical behavior of **1** towards *p*-quinones is completely different to that of the germene $Mes_2Ge=CR_2$. Whatever the quinone, similar reactions are observed leading to stable spiro compounds with four-membered oxagermacyclobutane rings. These results confirm the first step of the reaction postulated by calculations for germene and 1,4-benzoquinone.[5] Spiro compounds **2**–**5** do not undergo rearrangement in solution and the formation of five- or six-membered ring derivatives has not been observed. Another striking difference is the possibility to cleanly isolate a monocycloadduct, whereas a dicycloadduct was exclusively observed in the case of germene, even when using only one equivalent of the latter. However, a dicycloadduct can also be obtained by using two equivalents of **1**.

## 9,10-Phenanthrenequinone and Benzil

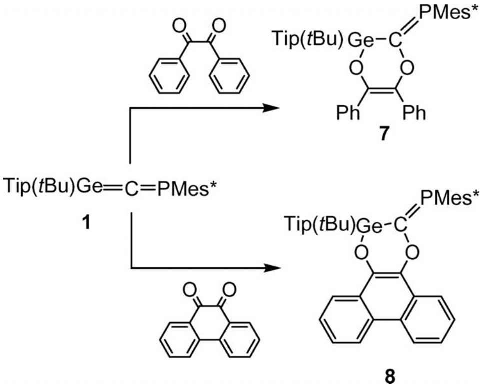
To continue the comparison with $Mes_2Ge=CR_2$, we have studied the reactivity towards **1** of the α-diketone benzil. We have also extended our study to include the *ortho*-quinone phenanthrenequinone. Benzil and phenanthrenequinone were added in equivalent molar ratios to solutions of **1** cooled to –80 °C to give the sole derivatives **7** and **8**, respectively, by a [2 + 4] cycloaddition between the Ge=C double bond and the O=C–C=O unit (Scheme 6). Their structures were determined by mass spectrometry [the presence of molecular peaks at 832 (for **7**) and 830 (for **8**)], which proves the formation of 1:1 adducts, and by NMR spectroscopy. $^{31}$P NMR spectra display signals at low field (**7**: 256.9 ppm and **8**: 265.5 ppm) indicating the presence of a P=C double bond, and $^{13}$C NMR spectra show signals corresponding to a O–C=C–O unit [**7**: C(OGe) 138.42 ppm, C(OCP) 142.23 ppm, $^{3}J_{CP}$ = 8.6 Hz; **8**: C(OGe) 138.42 ppm, C(OCP) 139.89 ppm, $^{3}J_{CP}$ = 7.8 Hz]. For the *o*-*t*Bu groups, two singlets are observed in $^{1}$H NMR and two doublets in $^{13}$C NMR due to the hindered rotation of the Mes* group on the NMR time scale. By contrast only one doublet is



Scheme 5. Synthesis of the cycloadduct **6**.

© 2011 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

observed for the diastereotopic methyl groups of the *p*-*i*Pr groups due to their distance from the chiral center. All these data are in agreement with [2 + 4] cycloadditions between the Ge=C double bonds and the O=C–C=O units.



Scheme 6. Reaction of **1** with 9,10-phenanthrenequinone and benzil.

The structures of **7** and **8** were unambiguously determined by an X-ray study, see Figures 2 (for **7**) and 3 (for **8**). The C=C double bond lengths [for **7**: 1.345(4) Å; for **8**: 1.353(3) Å] in the (O)C=C(O) unit, prove the formation of the six-membered Ge–O–C=C–O–C rings. **7** and **8** present some different characteristics: surprisingly, the configurations of the P=C double bonds are different (*Z* for **7** and *E* for **8**) without satisfactory explanation. In **8**, the four cycles of the phenanthrenic unit and of the dioxagermacyclohexene are in the same plane, with the sole exception of the germanium atom situated 0.432 Å out of the plane. In **7**, the six-membered Ge1–O1–C2–C9–O2–C1 ring is distorted; the Ge atom is close to the O1–C2–C9–O2 plane (0.267 Å), while the C1 atom is at 0.834 Å out of this plane. The phenyl groups are not coplanar with the O–C=C–O plane showing twists of 31.78° (Ph of COC) and 42.68° (Ph of COGe) preventing conjugation through the C=C double bond. Whereas in **8**, the P=C double bond is in the plane of the phenanthrenic unit, in fact, it is nearly perpendicular to the O–C=C–O plane in **7** (P1–C1–O2–C9 97.91°).

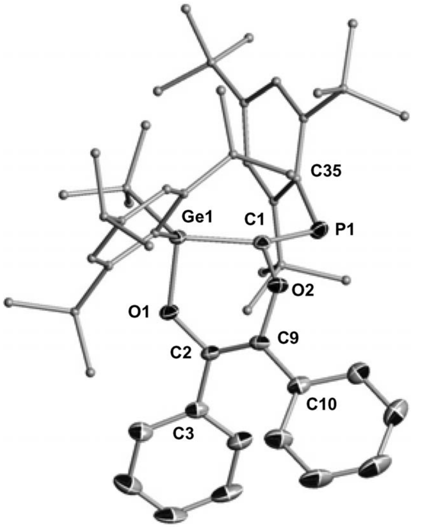


Figure 2. Structure of **7**. Thermal ellipsoids are drawn at the 50% probability level. A disorder of a *t*Bu group from Mes*, noncoordinating Me$_2$CO, and all hydrogen atoms are omitted. Tip, *t*Bu, and Mes* have been simplified for clarity. Selected bond lengths [Å] and angles [°]: Ge1–C1 1.970(2), C1–O2 1.436(3), O2–C9 1.418(3), C2–C9 1.345(4), O1–C2 1.375(3), Ge1–O1 1.830(2), P1–C1 1.686(2), P1–C35 1.854(3), O1–Ge1–C1 90.0(1), C2–O1–Ge1 120.4(2), C9–C2–O1 124.5(2), C2–C9–O2 121.4(2), C9–O2–C1 114.9(2), O2–C1–Ge1 100.8(2).

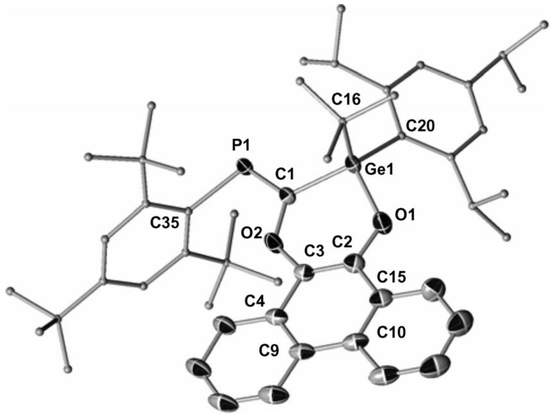
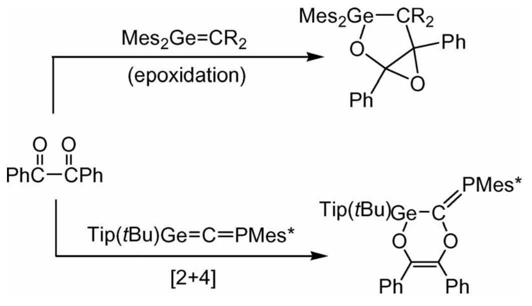


Figure 3. Structure of **8**. Thermal ellipsoids are drawn at the 50% probability level. Disorders of Tip and a *t*Bu group from Mes* and all hydrogen atoms are omitted. Tip, *t*Bu and Mes* have been simplified for clarity. Selected bond lengths [Å] and angles [°]: Ge1–C1 1.971(2), Ge1–C16 1.990(2), Ge1–C20 1.988(2), Ge1–O1 1.821(2), O1–C2 1.357(2), C2–C3 1.353(3), O2–C3 1.382(2), O2–C1 1.372(2), C2–C15 1.448(3), C10–C15 1.414(3), C9–C10 1.450(3), C4–C9 1.415(3), C3–C4 1.439(3), P1–C1 1.686(2), P1–C35 1.861(2), O1–Ge1–C1 96.79(7), C2–O1–Ge1 122.8(2), C3–C2–O1 124.8(2), C2–C3–O2 125.7(2), C1–O2–C3 126.2(2), O2–C1–Ge1 118.0(2).

We must note that the reactions of **1** and germene Mes$_2$Ge=CR$_2$ towards benzil are completely different as with the germene an epoxidation was observed (Scheme 3 and Scheme 7). The first steps of the reaction are probably the same, involving a nucleophilic attack of one oxygen atom on the germanium. In the case of **7**, the ring closure leading to the six-membered ring could be faster than the epoxidation, whereas with the germene, due to good stabilization of the anionic charge on the fluorenyl group, the epoxidation is favored.



Scheme 7. Different reactivities of Mes$_2$Ge=CR$_2$ and **1** towards benzil.

© 2011 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

The reactivity of **1** towards benzil is similar to that observed for silenes >Si=C<,[15] phosphagermene –P=Ge<,[16] and germavinylidene >C=Ge:[17] with this diketone.

## Conclusions

Although **1** reacts with *o*- and *p*-quinones and α-diketones exclusively through the Ge=C double bond, its chemical behavior is completely different to that of the germene $Mes_2Ge=CR_2$. This difference is due, among other factors, to the presence of the cumulated P=C double bond and a less polarized Ge=C double bond in **1**. Regioselective and nearly quantitative reactions are observed, which prove the high synthetic potential of this heteroallene in organometallic and heterocyclic chemistry.

## Experimental Section

**General Information:** 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 $CDCl_3$ as solvent) with a Bruker Avance 300 spectrometer at the following frequencies: $^{1}H$, 300.13 MHz (reference TMS); $^{13}C$, 75.47 MHz (reference TMS); $^{31}P$, 121.51 MHz (reference $H_3PO_4$). $^{1}H$ and $^{13}C\{^{1}H\}$ NMR assignments were confirmed by $^{1}H$ COSY, HSQC ($^{1}H$-$^{13}C$), and HMBC ($^{1}H$-$^{13}C$) experiments. Melting points were determined with a Wild Leitz-Biomed apparatus. Mass spectra were obtained with a Hewlett–Packard 5989A spectrometer by EI at 70 eV and with a Nermag R10-10 spectrometer by CI. Elemental analyses were performed by the Service de Microanalyse de l'Ecole de Chimie de Toulouse.

**Synthesis of 1:** The phosphagermaallene **1** was synthesized as described previously[11a] by addition of one equivalent of *tert*-butyllithium to an $Et_2O$ solution of phosphagermapropene Tip(*t*Bu)(F)-Ge–C(Cl)=PMes* cooled to –80 °C. As the reaction was quantitative according to $^{31}P$ NMR spectra, crude brown-red solutions of **1**, including LiF, were used in all cases.

**Reaction of *p*-Quinones with 1:** To a solution of **1** (1 mmol) in $Et_2O$ (20 mL) cooled to –80 °C was added one equivalent of *p*-quinone (1,4-benzoquinone, 2,3,5,6-tetramethyl-1,4-benzoquinone, 1,4-naphthoquinone, and 9,10-anthraquinone). After warming to room temperature and stirring for 3 h, a yellow coloration appeared. Solvents were removed in vacuo and replaced by pentane (50 mL). LiF was removed by filtration. After concentration to 5 mL, cooling to –20 °C afforded crystals of derivatives **2**, **3**, **4**, and **5**.

**2:** Yield 0.57 g, 78 %, m.p. 123 °C. $^{1}H$ NMR (300.13 MHz, $CDCl_3$): $\delta$ = 0.37, 0.94, 1.12 and 1.29 (4d, $^{3}J_{HH}$ = 6.6 Hz, 4 × 3 H, *o*-CH*MeMe*′), 1.22 (d, $^{3}J_{HH}$ = 6.6 Hz, 6 H, *p*-CH*MeMe*′), 1.26 (s, 9 H, GeCMe$_3$), 1.30 (s, 9 H, *p*-CMe$_3$ of Mes*), 1.32 and 1.56 (2s, 2 × 9 H, *o*-CMe$_3$ of Mes*), 1.88 and 3.58 (2sept, $^{3}J_{HH}$ = 6.6 Hz, 2 × 1 H, *o*-C*H*MeMe′), 2.82 (sept, $^{3}J_{HH}$ = 6.6 Hz, 1 H, *p*-C*H*MeMe′), 6.03 and 6.21 ($^{3}J_{HH}$ = 10.2, $^{4}J_{HH}$ = 1.8 Hz, 2 × 1 H, CHC=O), 6.79 and 7.04 (2s, 2 × 1 H, *m*-CH of Tip), 6.99 and 7.38 ($^{3}J_{HH}$ = 10.2, $^{4}J_{HH}$ = 3.0 Hz, 2 × 1 H, CHC-O), 7.34 and 7.42 (2s, 2 × 1 H, *m*-CH of Mes*) ppm. $^{13}C$ NMR (75.47 MHz): $\delta$ = 23.76 (*p*-CH*MeMe*′), 23.87, 24.78, 25.61 and 27.27 (*o*-CH*MeMe*′), 27.91 (GeC*Me*$_3$), 31.31 (*p*-C*Me*$_3$ of Mes*), 31.82 and 37.92 (*o*-*C*HMeMe′), 33.38 (d, $^{4}J_{CP}$ = 8.4 Hz) and 34.45 (d, $^{4}J_{CP}$ = 5.4 Hz, *o*-C*Me*$_3$ of Mes*), 34.13 (*p*-*C*HMeMe′), 35.05 (*p*-*C*Me$_3$ of Mes*), 35.96 (Ge*C*Me$_3$), 38.21 and 38.98 (*o*-*C*Me$_3$ of Mes*), 86.75 (d, $^{2}J_{CP}$ = 41.6 Hz, C-O), 120.85, 122.23, 122.36 and 123.02 (*m*-CH of Tip. *m*-CH of Mes*), 122.85 (d, $^{4}J_{CP}$ = 2.9 Hz) and 125.48 (d, $^{4}J_{CP}$ = 3.0 Hz, *C*HC=O), 130.18 (*ipso*-C of Tip), 135.15 (d, $^{1}J_{CP}$ = 68.38 Hz, *ipso*-C of Mes*), 150.00 (d, $^{3}J_{CP}$ = 7.3 Hz) and 153.33 (d, $^{3}J_{CP}$ = 7.3 Hz, CHC-O), 150.56 and 151.08 (*p*-C of Mes* and *p*-C of Tip), 152.81, 153.28, 153.44 (d, $^{2}J_{CP}$ = 8.7 Hz) and 155.69 (*o*-C of Mes* and *o*-C of Tip), 185.76 (d, $^{1}J_{CP}$ = 64.15 Hz, C=P), 186.84 (C=O) ppm. $^{31}P$ NMR (121.51 MHz): $\delta$ = 336.3 ppm. MS: *m*/*z* (%) = 731 (5) [M + 1], 674 (5) [M – *t*Bu + 1], 509 (10) [Tip(*t*Bu)-Ge=C=PMes* – 2*t*Bu + 1], 276 (5) [TipGe – 1], 57 (100) [*t*Bu]. $C_{44}H_{65}GeO_2P$ (729.56): calcd. C 72.44, H 8.98; found C 72.62, H 9.05.

**3:** Yield 0.60 g, 77 %, m.p. 145 °C. $^{1}H$ NMR (300.13 MHz, $CDCl_3$): $\delta$ = 0.45, 0.94, 1.24 and 1.28 (4d, $^{3}J_{HH}$ = 6.6 Hz, 4 × 3 H, *o*-CH*MeMe*′), 1.18 (s, 9 H, Ge-CMe$_3$), 1.20 (d, $^{3}J_{HH}$ = 6.6 Hz, 6 H, *p*-CH*Me*$_2$), 1.33 (s, 9 H, *p*-CMe$_3$ of Mes*), 1.34 and 1.43 (2s, 2 × 9 H, *o*-CMe$_3$ of Mes*), 1.83 (s, 6 H, MeC=CMe), 1.97 and 2.34 (2s, 4 × 3 H, MeC=CMe), 2.36 and 3.00 (2sept, $^{3}J_{HH}$ = 6.6 Hz, 2 × 1 H, *o*-C*H*MeMe′), 2.81 (sept, $^{3}J_{HH}$ = 6.6 Hz, 1 H, *p*-C*H*Me$_2$), 6.84 and 7.00 (2s, 2 × 1 H, *m*-CH of Tip), 7.33 and 7.37 (2s, 2 × 1 H, *m*-CH of Mes*) ppm. $^{13}C$ NMR (75.47 MHz): $\delta$ = 11.26, 11.51, 18.40 and 18.57 (*Me*C=C*Me*), 23.76, 25.16, 25.54 and 26.30 (*p*-CH*Me*$_2$, *o*-CH*MeMe*′), 30.00 (Ge-C*Me*$_3$), 31.30 (*p*-C*Me*$_3$ of Mes*), 33.45, 33.61 and 33.99 (*p*-CHMe$_2$, *o*-CHMeMe′), 33.79 (d, $^{4}J_{CP}$ = 8.8 Hz, *o*-C*Me*$_3$ of Mes*), 34.79 (*p*-*C*Me$_3$ of Mes*), 35.05 (Ge-*C*Me$_3$), 35.66 (d, $^{4}J_{CP}$ = 6.2 Hz, *o*-C*Me*$_3$ of Mes*), 38.39 and 39.66 (*o*-*C*Me$_3$ of Mes*), 93.50 (d, $^{2}J_{CP}$ = 39.0 Hz, C-O), 121.02 and 122.43 (m-CH of Tip), 121.52 and 122.95 (m-CH of Mes*), 127.22 (d, $^{4}J_{CP}$ = 2.5 Hz) and 129.13 (d, $^{4}J_{CP}$ = 4.0 Hz, *C*-C=O), 133.69 (d, $^{1}J_{CP}$ = 69.9 Hz, *ipso*-C of Mes*), 134.87 (*ipso*-C of Tip), 149.75 (*p*-C of Mes*), 150.16 (*p*-C of Tip), 151.30 and 153.20 (*o*-C of Tip), 153.35 (d, $^{2}J_{CP}$ = 5.9 Hz) and 154.17 (*o*-C of Mes*), 155.35 and 157.72 (2d, $^{3}J_{CP}$ = 7.7 Hz, *C*-C-O), 185.89 (C=O), 188.48 (d, $^{1}J_{CP}$ = 67.2 Hz, C=P) ppm. $^{31}P$ NMR (121.51 MHz): $\delta$ = 333.4 ppm. MS: *m*/*z* (%) = 786 (5) [M], 621 (5) [Tip(*t*Bu)Ge=C=PMes* – 1], 509 (10) [Tip(*t*Bu)Ge=C=PMes* – 2*t*Bu + 1], 377 (10) [Tip(*t*Bu)Ge=C=PMes* – Mes*], 276 (25) [TipGe – 1], 164 (20) [quinone], 57 (100) [*t*Bu]. $C_{48}H_{73}GeO_2P$ (785.67): calcd. C 73.38, H 9.37; found C 73.45, H 9.29.

**4:** Yield 0.53 g, 68 %, m.p. 174 °C. $^{1}H$ NMR (300.13 MHz, $CDCl_3$): $\delta$ = 0.84, 0.90, 1.13 and 1.27 (4d, $^{3}J_{HH}$ = 6.6 Hz, 4 × 3 H, *o*-CH*MeMe*′), 1.24 (d, $^{3}J_{HH}$ = 6.6 Hz, 6 H, *p*-CH*MeMe*′), 1.28 (s, 9 H, GeCMe$_3$), 1.32 and 1.42 (2s, 2 × 9 H, *o*-CMe$_3$ of Mes*), 1.33 (*p*-CMe$_3$ of Mes*), 1.96 and 3.38 (2sept, $^{3}J_{HH}$ = 6.6 Hz, 2 × 1 H, *o*-C*H*MeMe′), 2.86 (sept, $^{3}J_{HH}$ = 6.6 Hz, 1 H, *p*-C*H*MeMe′), 6.10 (d, $^{3}J_{HH}$ = 10.2 Hz, 1 H, CHC=O), 6.88 and 7.08 (2d, $^{4}J_{HH}$ = 1.5 Hz, 2 × 1 H, *m*-CH of Tip), 6.96 (d, $^{3}J_{HH}$ = 10.2 Hz, 1 H, CHC-O), 7.29 and 7.35 (2s, 2 × 1 H, *m*-CH of Mes*), 7.44 and 7.65 (2dt, = 7.5, $^{4}J_{HH}$ = 1.5 Hz, 2 × 1 H, arom. H), 8.12 (d, $^{3}J_{HH}$ = 7.5 Hz, 2 H, arom. H) ppm. $^{13}C$ NMR (75.47 MHz): $\delta$ = 23.73 and 23.84 (*p*-CH*MeMe*′), 24.83, 24.99, 25.59 and 27.41 (*o*-CH*MeMe*′), 28.55 (GeC*Me*$_3$), 31.37 (*p*-C*Me*$_3$ of Mes*), 32.74 and 36.45 (*o*-*C*HMeMe′), 34.02 (*p*-*C*HMeMe′), 34.56 (d, $^{4}J_{CP}$ = 8.2 Hz) and 35.14 (d, $^{4}J_{CP}$ = 5.7 Hz, *o*-C*Me*$_3$ of Mes*), 34.88 (*p*-*C*Me$_3$ of Mes*), 35.52 (Ge*C*Me$_3$), 38.34 and 39.12 (*o*-*C*Me$_3$ of Mes*), 87.77 (d, $^{2}J_{CP}$ = 38.6 Hz, C-O), 120.73 and 123.32 (*m*-CH of Tip), 121.03 and 122.42 (*m*-CH of Mes*), 122.16 (*C*HC=O), 125.90, 127.86, 128.97 and 132.63 (arom. CH), 130.47 and 148.48 (d, $^{3}J_{CP}$ = 7.5 Hz, arom. C), 131.98 (*ipso*-C of Tip), 135.27 (d, $^{1}J_{CP}$ = 65.5 Hz, *ipso*-C of Mes*), 149.83 (*p*-C of Tip), 150.77 (*p*-C of Mes*), 152.60

and 155.43 (*o*-C of Tip), 153.21 (d, $^{2}J_{CP}$ = 5.4 Hz) and 153.73 (*o*-C of Mes*), 154.30 (d, $^{3}J_{CP}$ = 8.5 Hz, *C*HC-O), 185.55 (C=O), 192.91 (d, $^{1}J_{CP}$ = 63.7 Hz, C=P) ppm. $^{31}$P NMR (121.51 MHz): $\delta$ = 328.2 ppm. MS: *m*/*z* (%) = 781 (5) [M + 1], 724 (10) [M – *t*Bu + 1], 377 (15) [Tip(*t*Bu)Ge=C=PMes* – Mes*], 275 (20) [TipGe – 2], 131 (10) [*t*BuGe], 57 (100) [*t*Bu]. $C_{48}H_{67}GeO_2P$ (779.62): calcd. C 73.95, H 8.66; found C 73.88, H 8.71.

**5:** Yield 0.59 g, 71%, m.p. 183 °C. $^{1}$H NMR (300.13 MHz, CDCl$_3$): $\delta$ = 0.66, 1.04, 1.28 and 1.39 (4d, $^{3}J_{HH}$ = 6.6 Hz, 4×3 H, *o*-CH*MeMe′*), 0.85 and 1.13 (2s, 2×9 H, *o*-CMe$_3$ of Mes*), 1.22 (s, 9 H, GeCMe$_3$), 1.26 (s, 9 H, *p*-CMe$_3$ of Mes*), 1.28 (d, $^{3}J_{HH}$ = 6.6 Hz, 6 H, *p*-CH*MeMe′*), 1.97 and 3.16 (2sept, $^{3}J_{HH}$ = 6.6 Hz, 2×1 H, *o*-C*H*MeMe′), 2.91 (sept, $^{3}J_{HH}$ = 6.6 Hz, 1 H, *p*-C*H*MeMe′), 6.92 and 7.16 (2d, $^{4}J_{HH}$ = 1.8 Hz, 2×1 H, *m*-CH of Tip), 7.00, 7.21, 7.48 and 7.69 (4ddd, $^{3}J_{HH}$ = 7.8, $^{3}J_{HH}$ = 7.2, $^{4}J_{HH}$ = 1.5 Hz, 4×1 H, arom. H), 7.16 and 7.22 (2s, 2×1 H, *m*-CH of Mes*), 7.52, 8.23, 8.30 and 8.45 (4dd, $^{3}J_{HH}$ = 7.8, $^{4}J_{HH}$ = 1.5 Hz, 4×1 H, arom. H) ppm. $^{13}$C NMR (75.47 MHz): $\delta$ = 23.90 and 23.95 (*p*-CH*MeMe′*), 24.53, 25.67, 25.79 and 27.46 (*o*-CH*MeMe′*), 29.05 (GeC*Me*$_3$), 31.36 (*p*-C*Me*$_3$ of Mes*), 33.75 (Ge*C*Me$_3$), 33.85 (d, $^{4}J_{CP}$ = 7.2 Hz) and 34.99 (d, $^{4}J_{CP}$ = 6.4 Hz, *o*-C*Me*$_3$ of Mes*), 34.19 (*p*-*C*HMeMe′), 34.39 and 35.25 (*o*-*C*HMeMe′), 34.75 (*p*-*C*Me$_3$ of Mes*), 37.87 and 39.23 (*o*-*C*Me$_3$ of Mes*), 91.01 (d, $^{2}J_{CP}$ = 32.7 Hz, C-O), 120.31 and 122.23 (*m*-CH of Mes*), 120.82 and 122.90 (*m*-CH of Tip), 125.74, 126.28, 126.49, 126.58, 127.23, 127.70, 132.24 and 132.25 (arom. CH), 129.64 (d, $J_{CP}$ = 2.7 Hz), 130.94 (d, $J_{CP}$ = 5.6 Hz), 149.54 (d, $J_{CP}$ = 2.5 Hz) and 150.28 (d, $J_{CP}$ = 7.4 Hz, arom. C), 134.03 (d, $^{1}J_{CP}$ = 63.3 Hz, *ipso*-C of Mes*), 134.52 (*ipso*-C of Tip), 149.52 (*p*-C of Mes*), 150.69 (*p*-C of Tip), 152.31 and 154.49 (*o*-C of Tip), 153.59 (d, $^{2}J_{CP}$ = 3.2 Hz) and 153.75 (*o*-C of Mes*), 185.12 (C=O), 195.36 (d, $^{1}J_{CP}$ = 62.1 Hz, C=P) ppm. $^{31}$P NMR (121.51 MHz): $\delta$ = 334.9 ppm. MS: *m*/*z* (%) = 831 (4) [M + 1], 774 (5) [M – *t*Bu + 1], 566 (15) [Tip(*t*Bu)Ge=C=PMes* – *t*Bu + 1], 510 (30) [Tip(*t*Bu)Ge=C=PMes* – 2*t*Bu + 2], 377 (10) [Tip(*t*Bu)Ge=C=PMes* – Mes*], 275 (15) [TipGe – 2], 208 (50) [1,4-anthraquinone], 131 (5) [*t*BuGe], 57 (100) [*t*Bu]. $C_{52}H_{69}GeO_2P$ (829.68): calcd. C 75.28, H 8.38; found C 75.36, H 8.27.

**Reaction of 1,4-Benzoquinone with 1 in a 1:2 Ratio:** The reaction is made exactly in the same conditions as described above for the 1:1 ratio reaction. Compound **1** (1 mmol) and *p*-benzoquinone (0.5 mmol) were reacted together to afford **6** (1.00 g; 74%; m.p. 197 °C). Compound **6** can be obtained by addition of one equivalent of **1** in Et$_2$O solution to the spiro compound **2** (0.51 g, 0.70 mmol) cooled to –50 °C. After warming to room temperature, the solvent was removed under reduced pressure and replaced by pentane (20 mL). LiF was removed by filtration, and cooling to –20 °C afforded **6** (0.76 g, 81%) in high purity. $^{1}$H NMR (300.13 MHz, CDCl$_3$): $\delta$ = 0.39, 0.93, 1.03 and 1.29 (4d, $^{3}J_{HH}$ = 6.6 Hz, 4×6 H, *o*-CH*MeMe′*), 1.19 (s, 18 H, Ge-CMe$_3$), 1.20 and 1.21 (2d, $^{3}J_{HH}$ = 6.6 Hz, 2×6 H, *p*-CH*MeMe′*), 1.33 (s, 18 H, *p*-CMe$_3$ of Mes*), 1.36 and 1.59 (2s, 2×18 H, *o*-CMe$_3$ of Mes*), 1.98 and 3.84 (2sept, $^{3}J_{HH}$ = 6.6 Hz, 2×2 H, *o*-C*H*MeMe′), 2.81 (sept, $^{3}J_{HH}$ = 6.6 Hz, 2 H, *p*-C*H*MeMe′), 6.13 and 6.30 (2dd, $^{3}J_{HH}$ = 9.9, $^{4}J_{HH}$ = 2.1 Hz, 2×2 H, CH-CO), 6.76 and 7.00 (2d, $^{4}J_{HH}$ = 1.5 Hz, 2×2 H, *m*-CH of Tip), 7.33 and 7.40 (2s, 2×2 H, *m*-CH of Mes*) ppm. $^{13}$C NMR (75.47 MHz): $\delta$ = 23.76 and 23.79 (*p*-CH*MeMe′*), 23.91, 24.88, 25.69 and 27.39 (*o*-CH*MeMe′*), 28.25 (Ge-C*Me*$_3$), 31.18 and 37.23 (*o*-*C*HMeMe′), 31.37 (*p*-C*Me*$_3$ of Mes*), 33.35 (d, $^{4}J_{CP}$ = 8.1 Hz) and 34.25 (d, $^{4}J_{CP}$ = 5.6 Hz, *o*-C*Me*$_3$ of Mes*), 34.05 (*p*-*C*HMeMe′), 34.74 (Ge-*C*Me$_3$), 34.95 (*p*-*C*Me$_3$ of Mes*), 38.28 and 38.92 (*o*-*C*Me$_3$ of Mes*), 86.25 (d, $^{2}J_{CP}$ = 40.8 Hz, C-O), 120.33 and 122.55 (*m*-CH of Tip), 121.73 and 121.95 (*m*-CH of Mes*), 129.66 (d, $^{3}J_{CP}$ = 7.8 Hz) and 134.87 (d, $^{3}J_{CP}$ = 8.5 Hz, *C*H-C-O), 131.72 (*ipso*-C of Tip), 138.22 (d, $^{1}J_{CP}$ = 71.7 Hz, *ipso*-C of Mes*), 149.29 (*p*-C of Mes*), 150.03 (*p*-C of Tip), 152.78 and 156.18 (*o*-C of Tip), 152.89 and 153.17 (d, $^{2}J_{CP}$ = 6.7 Hz), 195.80 (d, $^{1}J_{CP}$ = 66.7 Hz, C=P) ppm. $^{31}$P NMR (121.51 MHz): $\delta$ = 323.5 ppm. $C_{82}H_{126}Ge_2O_2P_2$ (1351.02): calcd. C 72.90, H 9.40; found C 73.01, H 9.35.

**Reaction of Benzil with 1:** A solution of benzil (1 mmol) in Et$_2$O (10 mL) was slowly added to a solution of **1** cooled to –80 °C. The reaction mixture, warmed to room temperature and stirred overnight, became yellow. Solvents were removed in vacuo and replaced by pentane (30 mL). LiF was removed by filtration. Crystallization from pentane at –20 °C afforded **7** (0.70 g, 84%, m.p. 201 °C). $^{1}$H NMR (300.13 MHz, CDCl$_3$): $\delta$ = 0.69 (s, 9 H, GeCMe$_3$), 1.22 (d, $^{3}J_{HH}$ = 6.9 Hz, 6 H, *p*-CH*Me*$_2$), 1.24 and 1.26 (2d, $^{3}J_{HH}$ = 6.9 Hz, 2×6 H, *o*-CH*MeMe′*), 1.28 (*p*-CMe$_3$ of Mes*), 1.36 and 1.64 (2s, 2×9 H, *o*-CMe$_3$ of Mes*), 2.81 (sept, $^{3}J_{HH}$ = 6.9 Hz, 1 H, *p*-C*H*Me$_2$), 3.29 (br., 2 H, *o*-C*H*MeMe′), 6.97 (s, 2 H, *m*-CH of Tip), 7.10–7.19 (m, 6 H, CH arom. of Ph), 7.33 and 7.40 (2s, 2×1 H, *m*-CH of Mes*), 7.33–7.36 (m, 2 H, CH arom. of Ph), 7.53 (d, $^{3}J_{HH}$ = 7.5 Hz, 2 H, CH arom. of Ph) ppm. $^{13}$C NMR (75.47 MHz): $\delta$ = 23.72 (*p*-CH*Me*$_2$), 24.92 and 26.23 (br., *o*-CH*MeMe′*), 27.62 (GeC*Me*$_3$), 29.14 (Ge*C*Me$_3$), 31.35 (*p*-C*Me*$_3$ of Mes*), 33.87 (*p*-*C*HMeMe′), 33.90 (*o*-*C*HMeMe′), 34.11 (d, $^{4}J_{CP}$ = 8.7 Hz) and 34.45 (d, $^{4}J_{CP}$ = 6.2 Hz, o-C*Me*$_3$ of Mes*), 34.79 (*p*-*C*Me$_3$ of Mes*), 38.77 and 38.82 (*o*-*C*Me$_3$ of Mes*), 122.23 (*m*-CH of Tip), 122.25 and 122.62 (*m*-CH of Mes*), 126.53, 126.68, 126.92 (2CH), 127.65 (2CH), 129.73 (2CH), 129.86 and 129.89 (arom. CH of Ph), 129.09, 129.34 (*ipso*-C of Tip, *ipso*-C of Mes*), 136.54, 137.70 and 138.42 (COGe and 2 *ipso*-C of Ph), 142.23 (d, $^{3}J_{CP}$ = 8.6 Hz, *C*OCP), 149.45 (*p*-C of Tip), 149.98 (*p*-C of Mes*), 154.54 (br., 2 *o*-C of Tip), 155.43 and 156.21 (d, $^{2}J_{CP}$ = 3.3 Hz, *o*-C of Mes*), 201.70 (d, $^{1}J_{CP}$ = 58.9 Hz, C=P) ppm. $^{31}$P NMR (121.51 MHz): $\delta$ = 256.9 ppm. MS: *m*/*z* (%) = 832 (5) [M], 775 (10) [M – *t*Bu], 565 (20) [Tip(*t*Bu)Ge=C=PMes* – *t*Bu], 377 (20) [Tip(*t*Bu)Ge=C=PMes* – Mes*], 333 (5) [Tip(*t*Bu)Ge – 1], 275 (50) [TipGe – 2], 203 (10) [Tip], 77 (70) [Ph], 57 (100) [*t*Bu]. $C_{52}H_{71}GeO_2P$ (831.72): calcd. C 75.10, H 8.60; found C 75.12, H 8.56.

**Reaction of 9,10-Phenanthrenequinone with 1:** A suspension of 9,10-phenanthrenequinone (1 mmol) in toluene (10 mL) was slowly added to a solution of **1** (1 mmol) in Et$_2$O (10 mL) cooled to –78 °C. After warming to room temperature, the yellow reaction mixture was stirred overnight. LiF was removed by filtration, and the solvents removed in vacuo and replaced with pentane (20 mL). Crystallization from cold pentane afforded **8** (0.74 g, 89%, m.p. 226 °C). $^{1}$H NMR (300.13 MHz, CDCl$_3$): $\delta$ = 0.79 and 1.29 (2d, $^{3}J_{HH}$ = 6.6 Hz, 2×6 H, *o*-CH*MeMe′*), 0.83 (s, 9 H, GeCMe$_3$), 1.14 and 1.66 (2s, 2×9 H, *o*-CMe$_3$ of Mes*), 1.16 (d, $^{3}J_{HH}$ = 6.9 Hz, 6 H, *p*-CH*MeMe′*), 2.75 (sept, $^{3}J_{HH}$ = 6.6 Hz, 1 H, *p*-C*H*MeMe′), 3.24 (br. s, 2 H, *o*-C*H*MeMe′), 6.88 (s, 2 H, *m*-CH of Tip), 7.36 and 7.42 (2s, 2×1 H, *m*-CH of Mes*), 7.46 (dt, $^{3}J_{HH}$ = 7.5, $^{4}J_{HH}$ = 1.2 Hz, 1 H), 7.53–7.59 (m, 3 H), 8.30–8.33 (m, 1 H), 8.40 and 8.56 (2d, $^{3}J_{HH}$ = 8.1 Hz, 2 H), 8.54–8.57 (m, 1 H, arom. CH of phenanthrene unit) ppm. $^{13}$C NMR (75.47 MHz): $\delta$ = 23.60 and 23.71 (*p*-CH*MeMe′*), 24.73 and 25.94 (*o*-CH*MeMe′*), 27.92 (GeC*Me*$_3$), 29.29 (Ge*C*Me$_3$), 31.39 (*p*-C*Me*$_3$ of Mes*), 33.61 (*p*-*C*HMeMe′), 33.77 (d, $^{4}J_{CP}$ = 8.7 Hz) and 34.23 ($^{4}J_{CP}$ = 8.7 Hz, *o*-C*Me*$_3$ of Mes*), 34.45 (2 *o*-*C*HMeMe′), 34.89 (*p*-*C*Me$_3$ of Mes*), 38.64 (2 *o*-*C*Me$_3$ of Mes*), 121.56, 122.05, 122.26, 122.67, 123.50, 124.72, 125.81 and 126.27 (arom. CH), 127.70, 127.72, 128.34 and 129.83 (arom. C), 129.17 (*ipso*-C of Tip), 129.58 (d, $^{1}J_{CP}$ = 62.43 Hz, *ipso*-C of Mes*), 138.42 (COGe), 139.89 (d, $^{3}J_{CP}$ = 7.8 Hz, *C*OCP), 149.65 and 150.24 (*p*-C of Tip and *p*-C of Mes*), 154.72 (br., *o*-C of Tip), 155.41 and 156.27 (d, $^2J_{CP}$ = 3.1 Hz, *o*-C of Mes*), 202.61 (d, $^1J_{CP}$ = 60.0 Hz, C=P) ppm. $^{31}$P NMR (121.51 MHz): $\delta$ = 265.5 ppm. MS: *m/z* (%) = 830 (10) [M], 773 (4) [M – *t*Bu], 715 (2) [M – 2*t*Bu – 1], 621 (2) [9,10-phenanthrenequinone – 1], 585 (4) [M – Mes*], 565 (15) [Tip(*t*Bu)Ge=C=PMes* – *t*Bu], 542 (10) [M – Mes*PC], 377 (10) [Tip(*t*Bu)Ge=C=PMes* – Mes*], 333 (5) [Tip(*t*Bu)Ge – 1], 275 (40) [TipGe – 2], 233 (20) [TipGe – *i*Pr], 131 (5) [*t*BuGe], 57 (100) [*t*Bu]. $C_{52}H_{69}GeO_2P$ (829.68): calcd. C 75.28, H 8.38; found C 75.33, H 8.41.

**X-ray Structure Determinations for 3, 7, and 8:** All data were collected at low temperatures using an oil-coated shock-cooled crystal with a Bruker AXS APEX II diffractometer with Mo-$K_\alpha$ radiation ($\lambda$ = 0.71073 Å). The structures were solved by direct methods[18], and all non-hydrogen atoms were refined anisotropically using the least-squares method on $F^2$.[19]

**3:** $C_{48}H_{73}GeO_2P$, *M* = 785.62, crystal size 0.4 × 0.4 × 0.1 mm$^3$, monoclinic, space group $P2_1/n$, *a* = 13.143(1) Å, *b* = 9.929(1) Å, *c* = 34.217(2) Å, $\beta$ = 93.33(1)°, *V* = 4457.6(2) Å$^3$, *Z* = 4, *T* = 180(2) K, 67191 reflections collected, 10898 unique reflections ($R_{int}$ = 0.0687), *R*1 = 0.0470, *wR*2 = 0.1052 [$I > 2\sigma(I)$], *R*1 = 0.0731, *wR*2 = 0.1154 (all data), residual electron density: 0.803 e Å$^{-3}$.

**7·CH$_3$COCH$_3$:** $C_{55}H_{77}GeO_3P$, *M* = 889.73, crystal size: 0.5 × 0.4 × 0.3 mm$^3$, orthorhombic, space group $Pna2_1$, *a* = 17.3423(5) Å, *b* = 21.8401(6) Å, *c* = 13.2244(3) Å, *V* = 5008.8(2) Å$^3$, *Z* = 4, *T* = 110(2) K, 46590 reflections collected, 10092 unique reflections ($R_{int}$ = 0.0377), *R*1 = 0.0349, *wR*2 = 0.0800 [$I > 2\sigma(I)$], *R*1 = 0.0471, *wR*2 = 0.0857 (all data), residual electron density = 0.749 e Å$^{-3}$.

**8:** $C_{52}H_{69}GeO_2P$, *M* = 829.63, crystal size: 0.4 × 0.3 × 0.3 mm$^3$, monoclinic, space group $P2_1/n$, *a* = 9.0123(3) Å, *b* = 28.0792(10) Å, *c* = 18.6998(7) Å, $\beta$ = 101.840(2)°, *V* = 4631.5(3) Å$^3$, *Z* = 4, *T* = 180(2) K, 48827 reflections collected, 11378 unique reflections ($R_{int}$ = 0.0552), *R*1 = 0.0402, *wR*2 = 0.0911 [$I > 2\sigma(I)$], *R*1 = 0.0611, *wR*2 = 0.0994 (all data), residual electron density: 0.373 e Å$^{-3}$.

CCDC-783545 (for **3**), -783546 (for **7**·CH$_3$COCH$_3$) and -783547 (for **8**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

## Acknowledgments

We are grateful to the Agence Nationale pour la Recherche (contract ANR-08-BLAN-0105-01) and PhoSciNet (CM0802) for financial support.

---

[1] For reviews, see: a) G. Raabe, J. Michl, *Chem. Rev.* **1985**, *85*, 419–509; b) A. G. Brook, M. Brook, *Adv. Organomet. Chem.* **1996**, *39*, 71–158; c) T. Müller, W. Ziche, N. Auner in *The Chemistry of Organosilicon Compounds*, vol. 2, part 2 (Eds.: Z. Rappoport, Y. Apeloig), Wiley, New York, **1998**, chapter 16; d) T. L. Morkin, W. J. Leigh, *Acc. Chem. Res.* **2001**, *34*, 129–136; e) T. L. Morkin, T. R. Owens, W. J. Leigh, in *The Chemistry of Organosilicon Compounds*, vol. 3 (Eds.: Z. Rappoport, Y. Apeloig), Wiley, New York, **2001**, chapter 17, p. 949–1026; f) L. E. Gusel'nikov, *Coord. Chem. Rev.* **2003**, *244*, 149–240; g) V. Ya. Lee, A. Sekiguchi, *Organometallics* **2004**, *23*, 2822–2834; h) H. Ottosson, P. G. Steel, *Chem. Eur. J.* **2006**, *12*, 1576–1585.

[2] For reviews, see: a) K. M. Baines, W. G. Stibbs, *Adv. Organomet. Chem.* **1996**, *39*, 275–324; b) J. Escudié, H. Ranaivonjatovo, *Adv. Organomet. Chem.* **1999**, *44*, 113–174; c) J. Escudié, C. Couret, H. Ranaivonjatovo, J. Satgé, *Coord. Chem. Rev.* **1994**, *130*, 427–480; d) N. Tokitoh, R. Okazaki, in: *The Chemistry of Organic Germanium, Tin and Lead Compounds*, vol. 2 (Eds.: Z. Rappoport), Wiley & Sons, New York, **2002**, chapter 13, p. 843–901.

[3] D. Ghereg, S. Ech-Cherif El Kettani, M. Lazraq, H. Ranaivonjatovo, W. W. Schoeller, J. Escudié, H. Gornitzka, *Chem. Commun.* **2009**, 4821–4823.

[4] D. Ghereg, H. Gornitzka, H. Ranaivonjatovo, J. Escudié, *Dalton Trans.* **2010**, *39*, 2016–2022.

[5] D. Ghereg, E. André, S. Ech-Cherif El Kettani, N. Saffon, M. Lazraq, H. Ranaivonjatovo, H. Gornitzka, K. Miqueu, J.-M. Sotiropoulos, J. Escudié, *Organometallics* **2010**, *29*, 4849–4857.

[6] S. Ech-Cherif El Kettani, M. Lazraq, F. Ouhsaine, H. Gornitzka, H. Ranaivonjatovo, J. Escudié, *Org. Biomol. Chem.* **2008**, *6*, 4064–4066.

[7] For reviews on heteroallenes, see: a) J. Escudié, H. Ranaivonjatovo, L. Rigon, *Chem. Rev.* **2000**, *100*, 3639–3696; b) B. Eichler, R. West, *Adv. Organomet. Chem.* **2001**, *46*, 1–46; c) J. Escudié, H. Ranaivonjatovo, *Organometallics* **2007**, *26*, 1542–1559; d) R. Appel, in: *Multiple Bonds and Low Coordination in Phosphorus Chemistry* (Eds.: M. Regitz, O. J. Scherer) Thieme, Stuttgart, **1990**, pp. 157–219; e) M. Yoshifuji, *J. Chem. Soc., Dalton Trans.* **1998**, 3343–3349.

[8] For stable >Si=C=C<, see: a) G. Miracle, J. L. Ball, D. R. Powell, R. West, *J. Am. Chem. Soc.* **1993**, *115*, 11598–11599; b) M. Trommer, G. E. Miracle, B. E. Eichler, D. R. Powell, R. West, *Organometallics* **1997**, *16*, 5737–5747; c) B. E. Eichler, G. E. Miracle, D. R. Powell, R. West, *Main Group Met. Chem.* **1999**, *22*, 147–162; d) M. Ichinohe, T. Tanaka, A. Sekiguchi, *Chem. Lett.* **2001**, 1074–1075; e) S. Spirk, F. Belaj, J. H. Albering, R. Pietschnig, *Organometallics* **2010**, *29*, 2981–2986.

[9] For stable >Ge=C=C<, see: a) B. E. Eichler, D. R. Powell, R. West, *Organometallics* **1998**, *17*, 2147–2148; B. E. Eichler, D. R. Powell, R. West, *Organometallics* **1999**, *18*, 540–545; b) K. Kishikawa, N. Tokitoh, R. Okazaki, *Organometallics* **1997**, *16*, 5127–5129; c) N. Tokitoh, K. Kishikawa, R. Okazaki, *Chem. Lett.* **1998**, 811–812.

[10] >Si=C=N–[10a–10c] and >Sn=C=N–[10d] are generally better considered as silylenes (or stannylenes) isocyanide complexes than as azasilaallenes (or azastannaallenes), see: a) N. Takeda, H. Suzuki, N. Tokitoh, R. Okazaki, S. Nagase, *J. Am. Chem. Soc.* **1997**, *119*, 1456–1457; b) N. Takeda, T. Kajiwara, H. Suzuki, R. Okazaki, N. Tokitoh, *Chem. Eur. J.* **2003**, *9*, 3530–3543; c) T. Abe, T. Iwamoto, C. Kabuto, M. Kira, *J. Am. Chem. Soc.* **2006**, *128*, 4228–4229; d) H. Grützmacher, S. Freitag, R. Herbst-Irmer, G. M. Sheldrick, *Angew. Chem. Int. Ed. Engl.* **1992**, *31*, 437–438.

[11] Only one >Ge=C=P– derivative[11a] is stable at room temperature, see: a) Y. El Harouch, H. Gornitzka, H. Ranaivonjatovo, J. Escudié, *J. Organomet. Chem.* **2002**, *643–644*, 202–208; transient >Si=C=P–[11b] and >Ge=C=P–[11c] have also been reported, see: b) L. Rigon, H. Ranaivonjatovo, J. Escudié, A. Dubourg, J.-P. Declercq, *Chem. Eur. J.* **1999**, *5*, 774–781; c) H. Ramdane, H. Ranaivonjatovo, J. Escudié, S. Mathieu, N. Knouzi, *Organometallics* **1996**, *15*, 3070–3075.

[12] For reviews on $^{31}$P chemical shifts, see: S. Lochschmidt, A. Schmidpeter, *Phosphorus Sulfur* **1986**, *29*, 73–109.

[13] a) K. M. Baines, W. G. Stibbs, *Coord. Chem. Rev.* **1995**, *145*, 157–200; b) C. E. Holloway, M. Melnik, *Main Group Met. Chem.* **2002**, *25*, 185–266.

[14] M. Lazraq, C. Couret, J. Escudié, J. Satgé, M. Draeger, *Organometallics* **1991**, *10*, 1771–1778.

[15] In the case of the silene $(Me_3Si)_2Si=C(OSiMe_3)R$ (R = *t*Bu, Ad) produced by photolysis, a [2 + 4] cycloaddition occurred between the Si=C double bond and the two C=O double bonds of benzil, see: A. Naka, M. Ishikawa, *J. Organomet. Chem.* **2003**, *685*, 162–167.

[16] A [2 + 4] cycloaddition leading to a six-membered ring derivative has also been reported between the Ge=P double bond of

the phosphagermene Mes*P=GeMes$_2$ and the two C=O double bonds of benzil, see: A. Kandri Rodi, J.-P. Declercq, A. Dubourg, H. Ranaivonjatovo, J. Escudié, *Organometallics* **1995**, *14*, 1954–1960.

[17] The transient germavinylidene [Me$_3$SiN=P(Ph$_2$)]$_2$C=Ge**:** possesses both a Ge=C double bond and a germylene function. Reaction with benzil occurs exclusively on the germanium atom by a [1 + 4] cycloaddition, and the Ge=C double bond is not involved, see: W.-P. Leung, K.-W. Kan, C.-W. So, T. C. W. Mak, *Organometallics* **2007**, *26*, 3802–3806.

[18] G. M. Sheldrick, *Acta Crystallogr., Sect. A* **1990**, *46*, 467–473.

[19] G. M. Sheldrick, *Acta Crystallogr., Sect. A* **2008**, *64*, 112–122.

Received: July 8, 2010

Published Online: December 7, 2010

© 2011 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim