# From a Phosphagermaallene −P=C=Ge< and Heavier Chalcogens (S, Se, Te): Access to 3-Phosphanylidene-1,2-Chalcogenagermiranes

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*Received November 26, 2008*

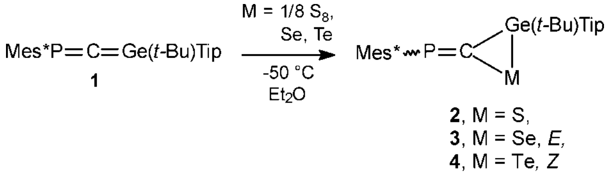
*Summary: Chalcogenagermiranes that feature an exocyclic P=C double bond were obtained from the phosphagermaallene Mes*P=C=Ge(t-Bu)Tip (Mes* = 2,4,6-tritert-butylphenyl, Tip = 2,4,6-triisopropylphenyl) and heavier chalcogens. The structural data of selena- and telluragermiranes show they are intermediate between a normal three-membered ring and a π-complex.*

Allenes play important role in organic chemistry. Their heavier congeners E=C=E′ (E, E′ = Si, Ge, Sn, N, P, As, O, S) have attracted considerable interest in recent years.[1] Indeed, such heavier heteroallenes appear to be valuable building blocks owing to the diversified reactivity of two double bonds.

Whereas many heteroallenes −P=C=E (E = C, N, P, As, O, S)[1] have been prepared, only a few stable heavier group 14 element-containing representatives of general formula $>E_{14}$=C=E ($E_{14}$ = Si, E = C,[2,3] E = N;[4] $E_{14}$ = Ge, E = C;[5] $E_{14}$ = Sn, E = N[6]) have been described, and their reactivity is still poorly documented. However, for E = N, the corresponding derivatives display important zwitterionic or silylene (or stannylene)-isocyanide contributions.

In the field of heteroallenes comprising two heavier elements of group 14 and 15 $-E_{15}$=C=$E_{14}$<, the transient phosphasilaallene Mes*P=C=Si(Ph)Tip (Mes* = 2,4,6-tritert-butylphenyl, Tip = 2,4,6-triisopropylphenyl)[7a] and the transient phosphagermaallene Mes*P=C=GeMes$_2$ (Mes = 2,4,6-trimethylphenyl)[7b] have been characterized only at low temperature by spectroscopic techniques as well as by trapping reactions. Attaching very bulky groups to both the germanium and the phosphorus atoms successfully led to the first stable 1,3-phosphagermaallene Mes*P=C=Ge(*t*-Bu)Tip **1**.[7c]

**Scheme 1**



(Mes* = 2,4,6-(*t*-Bu)$_3$C$_6$H$_2$, Tip = 2,4,6-iPr$_3$C$_6$H$_2$)

The steric protection in phosphagermaallene **1** seems particularly convenient for an efficient kinetic stabilization of strained Se- or Te-containing small ring compounds which are known to be generally labile.

Here we report on a thiagermirane and on its selenium and tellurium analogues, that feature an exocyclic P=C double bond. They were obtained from the phosphagermaallene Mes*P=C=Ge(*t*-Bu)Tip **1** and heavier chalcogens.

## Results and Discussion

Treatment of phosphagermaallene **1** with elemental sulfur, selenium, or tellurium in Et$_2$O at −50 °C gave in a good yield the unprecedented corresponding phosphanylidene-chalcogenagermiranes **2**−**4** that exhibit an exocyclic C=P double bond (Scheme 1).

Their structures were determined by $^1$H, $^{13}$C, $^{31}$P, $^{77}$Se, and $^{125}$Te NMR spectroscopies (**2**: $\delta^{31}P$ = 252.2 ppm; **3**: $\delta^{31}P$ = 278.8 ppm, $^{(2+3)}J_{PSe}$ = 107.5 Hz; **4**: $\delta^{31}P$ = 311.8 ppm, $^{(2+3)}J_{PTe}$ = 249.6 Hz) and by mass spectrometry. These large PSe and PTe coupling

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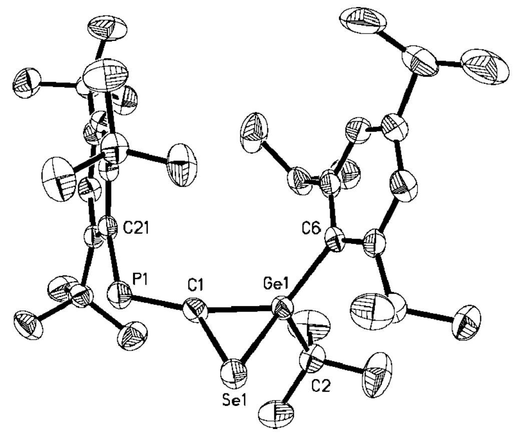

**Figure 1.** Molecular structure of **3**. Thermal ellipsoids are drawn at 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Ge1−C1 = 1.944(4); Ge1−C6 = 1.968(4); Ge1−C2 = 2.001(4); Ge1−Se1 = 2.3837(6); P1−C1 = 1.659(4); P1−C21 = 1.865(4); Se1−C1 = 1.951(4); C1−Ge1−C6 = 118.78(16); C1−Ge1−C2 = 120.74(17); C6−Ge1−C2 = 119.09(17); C1−Ge1−Se1 = 52.41(11); C6−Ge1−Se1 = 115.75(12); C2−Ge1−Se1 = 109.52(13); C1−P1−C21 = 107.26(18); C1−Se1−Ge1 = 52.12(11); P1−C1−Ge1 = 164.0(2); P1−C1−Se1 = 120.2(2); Ge1−C1−Se1 = 75.47(14).

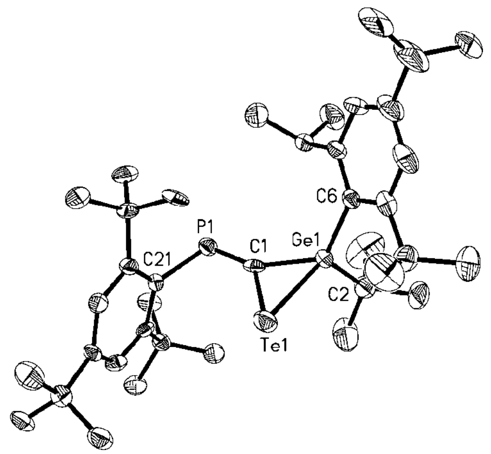

**Figure 2.** Molecular structure of **4**. Thermal ellipsoids are drawn at 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Ge1−C1 = 1.912(6); Ge1−Te1 = 2.5887(9); C1−Te1 = 2.122(6); C1−P1 = 1.666(7); Ge1−C6 = 1.957(6); Ge1−C2 = 1.969(8); P1−C21 = 1.856(6); Ge1−C1−Te1 = 79.6(2); Ge1−Te1−C1 = 46.60(17); C1−Ge1−Te1 = 53.76(19); C1−Ge1−C6 = 119.6(3); C6−Ge1−C2 = 117.7(3); C1−Ge1−C2 = 116.2(3); P1−C1−Te1 = 136.1(4); P1−C1−Ge1 = 144.3(4).

constants are greater than those found for selenadiphospholes (50−80 Hz)[8a−d] and telluradiphospholes (130−150 Hz).[8c,d] A $^2J_{\mathrm{PSe}}$ coupling constant of 98 Hz was reported in an acyclic P=C−Se unit.[8e]

The structures of the three-membered heterocycles **3** (Figure 1) and **4** (Figure 2) were confirmed by an X-ray analysis. Compound **4** adopts the Z configuration around the P=C double bond with the huge Mes* group in the cis disposition to the chalcogen atom whereas a trans disposition was observed for derivative **3** (Scheme 1). The origin for this surprising opposite arrangement is not clear at the moment.

Compound **4** is the first telluragermirane to be synthesized by a direct reaction between a germanium−carbon doubly bonded compound and elemental tellurium (a telluragermirane has been obtained by reaction between a germaallene and $\mathrm{R_3P{=}Te}$[5c]) whereas a thiagermirane and a selenagermirane bearing an exocyclic C=C double bond have been prepared from sulfur or selenium and the germaallene Tbt(Mes)Ge=C=$\mathrm{CR_2}$ ($\mathrm{CR_2}$ = fluorenylidene, Tbt = 2,4,6-$\mathrm{[(Me_3Si)_2CH]_3C_6H_2}$).[5c] All other thiagermiranes have been obtained by reaction between a germylene and thioketones.[9]

The Ge1−Se1 (2.3837(6) Å), C1−Se1 (1.951(4) Å), Ge1−Te1 (2.5887(9) Å), and C1−Te1 (2.122(6) Å) bond lengths in **3** and **4** are similar to those reported in a triselenagermole, (*d*GeSe = 2.402(1) Å) and (*d*CSe = 1.984(4) Å),[10] and in a telluragermirane, (*d*GeTe = 2.591(3) Å) and (*d*CTe = 2.11(2) Å).[5c] The exocyclic Ge−C bonds lengths for Ge−*t*-Bu and Ge−Tip (1.957(6) to 2.001(4) Å) lie in the normal range.[11] In contrast, the intracyclic Ge1−C1 bond length is slightly shortened in **3** (1.944(4) Å) and even more in **4** (1.912(6) Å) with large P1C1Ge1 bond angles in **3** (164.0(2)°) and in **4** (144.3(4)°). Moreover, the sum of the bond angles around the germanium atom (C1−Ge1−C6, C2−Ge1−C6 and C1−Ge1−C2) ignoring selenium (358.6° in **3**) or tellurium (353.5° in **4**) is close to 360°, showing that the germanium center displays some $\mathrm{sp^2}$ character. We can assume that this partially planar geometry corresponds to a structure intermediate between a normal three-membered ring and a $\pi$-complex.

Similar planar structures were found in other three-membered heterocycles containing one germanium atom such as GePS[12a] and GeCTe[5c] or two germanium atoms like GeGeX (X = C,[12b] N,[12b] S,[12c] Te,[12d]). These results can be interpreted in terms of Dewar-Chatt-Duncanson model of metal olefin bonding.

In conclusion, although **1** possesses two reactive double bonds, addition of chalcogens happened to take place selectively on the Ge=C unsaturation. This illustrates the synthetic potential of this heteroallene in organometallic and heterocyclic chemistry since the P=C unsaturation and the phosphorus lone pair remain available for a further reaction.

## Experimental Section

All experiments were carried out in flame-dried glassware under a nitrogen atmosphere using high-vacuum-line techniques. Solvents were dried and freshly distilled from sodium benzophenone and carefully deoxygenated on the vacuum line by several "freeze-pump-thaw" cycles. NMR spectra were recorded in $\mathrm{CDCl_3}$ on a Bruker Avance 300 spectrometer at the following frequencies: $^1$H, 300.13 MHz; $^{13}$C, 75.47 MHz (reference TMS); $^{31}$P, 121.51 MHz (reference $\mathrm{H_3PO_4}$); on a Bruker Avance 400 spectrometer for $^{77}$Se, 76.31 MHz (reference $\mathrm{Me_2Se}$) and on a Bruker Avance 500 spectrometer for $^{125}$Te, 175.85 MHz (reference $\mathrm{Me_2Te}$). Mass spectra were obtained on a Hewlett-Packard 5989A spectrometer by EI at 70 eV and on a Nermag R10−10 spectrometer by CI. Melting points were determined on a Wild Leitz-Biomed apparatus. Elemental analyses were performed by the Service de Microanalyse de l'Ecole de Chimie de Toulouse.

**3-(2,4,6-Triisopropylphenyl)-3-tert-butyl-1-(2,4,6-tritert-butylphenyl)phosphagermaallene 1.** Phosphagermaallene **1** was synthesized as previously described[7c] 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 (1.04 g, 1.54 mmol) in $\mathrm{Et_2O}$ (20 mL) cooled to −78 °C. A $^{31}$P NMR analysis ($\delta$ 249.9

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**Table 1. Crystal Data and Structure Refinement for 3 and 4**

| | **3** | **4** |
|---|---|---|
| Empirical formula | $C_{38}H_{61}GePSe$ | $C_{38}H_{61}GePTe$ |
| Formula weight | 700.39 | 749.03 |
| Crystal system | Triclinic | Monoclinic |
| Space group | $P\bar{1}$ | $P2_1/n$ |
| *a* (Å) | 9.5103(2) | 10.0341(3) |
| *b* (Å) | 11.9174(2) | 22.9800(8) |
| *c* (Å) | 17.9636(4) | 17.4571(6) |
| α (deg) | 83.2120(10) | 90.00 |
| *β* (deg) | 79.6660(10) | 103.726(3) |
| *γ* (deg) | 74.8620(10) | 90.00 |
| *V* (Å$^3$) | 1927.97(7) | 3910.4(2) |
| *Z* | 2 | 4 |
| Density (calculated) (g/cm$^3$) | 1.206 | 1.272 |
| Absorption coefficient $\mu$ (mm$^{-1}$) | 1.802 | 1.578 |
| *F*(000) | 740 | 1552 |
| Crystal size (mm) | 0.15 × 0.10 × 0.10 | 0.1 × 0.1 × 0.08 |
| Temperature (°C) | −80 | −80 |
| Scan mode | $\omega$, $\phi$ | $\omega$, $\phi$ |
| Detector | Bruker APEX II | Bruker APEX II |
| $\theta_{max}$ (deg) | 24.71 | 24.71 |
| no. obsd reflns | 24119 | 30121 |
| $R_{merge}$ | 0.0683 | 0.1622 |
| Data/restraints/parameters | 6497/78/414 | 6595/21/405 |
| *R* indices [$I > 2s(I)$] | $wR_2 = 0.0955$<br>$R_1 = 0.0443$ | $wR_2 = 0.0935$<br>$R_1 = 0.0514$ |
| *R* indices (all data) | $wR_2 = 0.1089$<br>$R_1 = 0.0794$ | $wR_2 = 0.1223$<br>$R_1 = 0.1396$ |
| max. diff peak, hole (e/Å$^3$) | 1.019, −0.355 | 0.561, −0.795 |

ppm) showed the nearly quantitative formation of phosphagermaallene **1**. Solutions of **1** were used directly without further purification.

**General Procedure for the Reaction of 1 with Chalcogens.** A crude solution of **1** prepared as previously described was cooled to −50 °C and was canulated into a flask, maintained at −50 °C, containing one equivalent of the heavier chalcogen. The reaction mixture rapidly turned brown (with sulfur), yellow-green (with selenium), or red (with tellurium) on warming to room temperature. After stirring overnight, it was black in all cases. The solvents were removed under vacuum and replaced by 20 mL of pentane. LiF was filtered out. Crystallization at −30 °C from pentane afforded crystals of **2**, **3**, or **4**.

**2:** white crystals, 0.85 g (89%), mp: 190 °C.

**$^1$H NMR.** $\delta$ 0.23 (broad s, $\Delta\nu_{1/2}$ = 15 Hz, 3H, *o*-CH*MeMe′* of Tip); 0.94−1.15 (m, 9H, *o*-CH*MeMe′* of Tip); 1.11 (d, $^3J_{HH}$ = 6.9 Hz, 6H, *p*-CH*MeMe′* of Tip); 1.16 (s, 9H, *o*-*t*-Bu of Mes*); 1.17 and 1.25 (2s, 2 × 9H, *t*-BuGe and *p*-*t*-Bu of Mes*); 1.54 (s, 9H, *o*-*t*-Bu of Mes*); 2.32 (broad s, $\Delta\nu_{1/2}$ = 22.4 Hz, 1H, *o*-C*H*MeMe′ of Tip); 2.73 (sept, $^3J_{HH}$ = 6.9 Hz, 1H, *p*-C*H*MeMe′ of Tip); 3.48 (broad s, $\Delta\nu_{1/2}$ = 22.5 Hz, 1H, *o*-C*H*MeMe′ of Tip); 6.71 and 6.88 (2 broad s, $\Delta\nu_{1/2}$ = 10.3 Hz, 2 × 1H, arom H of Tip); 7.24 and 7.36 (2 broad s, $\Delta\nu_{1/2}$ = 5.0 Hz, 2 × 1H, arom H of Mes*).

**$^{13}$C NMR.** $\delta$ 23.25 (broad s); 23.86; 23.95; 24.27 (broad s); 25.72 (broad s); 26.29 (broad s); 34.25; 36.46 (broad s) and 40.00 (broad s) (*o*-C*Me*$_3$ of *Mes**, CH and Me of $^i$Pr); 28.97 and 31.47 (GeC*Me*$_3$ and *p*-C*Me*$_3$); 33.40 (d, $J_{CP}$ = 8.4 Hz, *o*-C*Me*$_3$ of Mes*); 33.90 (d, $J_{CP}$ = 5.2 Hz, *o*-C*Me*$_3$ of Mes*); 34.44, 35.09, 38.28, and 38.94 (*C*Me$_3$ of *t*-Bu); 120.87 (broad s), 121.85 (broad s), 122.30 and 122.61 (broad s) (arom CH of Mes* and Tip); 128.59 (*ipso*-C of Tip); 139.55 (d, $^1J_{CP}$ = 66.7 Hz, *ipso*-C of Mes*); 149.55; 151.28; 153.56 (broad s); 153.71, 154.05 (d, $J_{CP}$ = 5.7 Hz) and 154.76 (broad s) (arom C of Mes* and Tip); 181.57 (d, $^1J_{CP}$ = 78.5 Hz, C=P).

**$^{31}$P NMR.** $\delta$ 252.2.

**MS (EI, 70 eV, *m/z*, %).** 654 (M$^+$, 2); 597 (M$^+$ − *t*-Bu, 75); 539 (M$^+$ − 2 *t*-Bu − 1, 4); 276 (Mes*P, 15); 57 (*t*-Bu, 100).

**MS (CI, CH$_4$, *m/z*, %).** 683 (M$^+$+ 29, 5); 655 (M$^+$ + 1, 75); 597 (M$^+$ − *t*-Bu, 100).

**Anal Calcd for $C_{38}H_{61}GePS$:** C, 69.84; H, 9.41. Found: C, 70.04; H, 9.60.

**3:** yellow crystals, 0.87 g (81%), mp: 147 °C.

**$^1$H NMR.** $\delta$ 0.17−0.25 (broad s, $\Delta\nu_{1/2}$ = 23 Hz, 3H, *o*-CH*MeMe′* of Tip); 0.78−1.3 (m, 9H, *o*-CH*MeMe′* of Tip); 1.11 (d, $^3J_{HH}$ = 6.8 Hz, 6H, *p*-CH*MeMe′* of Tip); 1.19 (s, 9H, *t*-BuGe or *p*-*t*-Bu of Mes*); 1.20 (s, 9H, *o*-*t*-Bu of Mes*); 1.24 (s, 9H, *t*-BuGe or *p*-*t*-Bu of Mes*); 1.54 (s, 9H, *o*-*t*-Bu of Mes*); 2.36 (broad s, $\Delta\nu_{1/2}$ = 23.8 Hz, 1H, *o*-C*H*MeMe′ of Tip); 2.73 (sept, $J_{HH}$ = 6.9 Hz, 1H, *p*-C*H*MeMe′ of Tip); 3.69 (broad s, $\Delta\nu_{1/2}$ = 25.6 Hz, 1H, *o*-C*H*MeMe′ of Tip); 6.74 and 6.88 (2 broad s, $\Delta\nu_{1/2}$ = 20 Hz, 2 × 1H, arom H of Tip); 7.24 and 7.36 (2s, 2 × 1H, arom H of Mes*).

**$^{13}$C NMR.** $\delta$ 23.81; 23.91; 24.19; 34.19 and 34.30 (*o*-C*Me*$_3$ of Mes*, CH and Me of $^i$Pr; some signals are too broad to be observed); 28.98 and 31.41 (GeC*Me*$_3$ and *p*-C*Me*$_3$); 33.45 (d, $J_{CP}$ = 8.6 Hz, *o*-C*Me*$_3$ of Mes*); 33.86 (d, $J_{CP}$ = 4.7 Hz, *o*-C*Me*$_3$ of Mes*); 35.09; 38.07; 38.86 (*C*Me$_3$ of *t*-Bu); 122.00 and 122.10 (arom CH of Mes*); 122.30 (arom CH of Tip); 128.04 (*ipso*-C of Tip); 142.01 (d, $^1J_{PC}$ = 73.8 Hz, *ipso*-C of Mes*); 148.69; 149.73; 151.14 and 153.09 (arom C of Tip and Mes*); 153.22 (d, $^2J_{PC}$ = 6.1 Hz *o*-C of Mes*); 174.57 (d, $^1J_{PC}$ = 87.7 Hz, C=P).

**$^{31}$P NMR.** $\delta$ 278.8 ($^{(2+3)}J_{PSe}$ = 107.5 Hz).

**$^{77}$Se NMR.** $\delta$ 103.7 (d, $^{(2+3)}J_{PSe}$ = 107.5 Hz).

**MS (EI, 70 eV, *m/z*, %).** 700 (M$^+$, 10); 643 (M$^+$ − *t*-Bu, 20); 275 (Mes*P − 1, 30); 57 (*t*-Bu, 100).

**Anal Calcd for $C_{38}H_{61}GePSe$:** C, 65.16; H, 8.78. Found: C, 65.42; H, 8.80.

**4:** orange crystals, 0.76 g (69%), mp: 180 °C.

**$^1$H NMR.** $\delta$ 1.04 (d, $J_{HH}$ = 6.5 Hz, 3H, *o*-CH*MeMe′* of Tip); 1.20 (d, $J_{HH}$ = 6.9 Hz, 6H, *p*-CH*MeMe’* of Tip); 1.23 (s, 9H, *t*-BuGe or *p*-*t*-Bu of Mes*); 1.25 (d, $^3J_{HH}$ = 6.7 Hz, 3H, *o*-CH*MeMe′* of Tip); 1.28 (s, 9H, *o*-*t*-Bu of Mes*); 1.32 (s, 9H, *t*-BuGe or *p*-*t*-Bu of Mes*); 1.34 (d, $^3J_{HH}$ = 6.5 Hz, 3H, *o*-CH*MeMe′* of Tip); 1.38 (d, $^3J_{HH}$ = 6.5 Hz, 3H, *o*-CH*MeMe′* of Tip); 1.48 (s, 9H, *o*-*t*-Bu of Mes*); 2.86 (sept, $^3J_{HH}$ = 6.9 Hz, 1H, C*H*MeMe′ of Tip), 3.49 (sept, $^3J_{HH}$ = 6.6 Hz, 1H, C*H*MeMe′ of Tip) and 3.74 (sept, $^3J_{HH}$ = 6.6 Hz, 1H, C*H*MeMe′ of Tip); 6.93 and 6.95 (AB type spectrum, $J_{HAHB}$ = 1.6 Hz, 2 × 1H, arom H of Tip); 7.32 and 7.37 (2 broad s, $\Delta\nu_{1/2}$ = 4.0 Hz, 2 × 1H, arom H of Mes*).

**$^{13}$C NMR.** $\delta$ 23.83; 23.94; 24.00; 24.18; 25.21; 25.90; 26.15; 34.19 and 38.53 (C*Me*$_3$, CH and Me of $^i$Pr); 29.80 and 31.40 (GeC*Me*$_3$ and *p*-C*Me*$_3$); 32.64 (d, $J_{CP}$ = 7 Hz, *o*-C*Me*$_3$ of Mes*); 33.35 (d, $J_{CP}$ = 7.1 Hz, *o*-C*Me*$_3$ of Mes*); 35.03 and 37.94 (*C*Me$_3$ of *t*-Bu); 121.40; 122.07; 122.36; 122.72 (arom CH of Mes* and Tip); 129.60 (*ipso*-C of Tip); 148.88; 150.88; 151.52; 151.75; 153.28; 154.48 (arom C of Mes* and Tip); 155.46 (d, $^1J_{CP}$ = 89 Hz, C=P).

**$^{31}$P NMR.** $\delta$ 311.8. ($^{(2+3)}J_{PTe}$ = 249.6 Hz).

**$^{125}$Te NMR.** $\delta$ −10.9 (d, $^{(2+3)}J_{PTe}$ = 249.6 Hz).

**MS (EI, 70 eV, *m/z*, %).** 750 (M$^+$, 3); 691 (M$^+$ − *t*-Bu − 2, 20); 635 (M$^+$ − 2 *t*-Bu − 1, 1); 563 (M$^+$ − Te – *t*-Bu − 2, 2); 333 (Tip(*t*-Bu)Ge − 1, 10); 275 (Mes*P − 1, 15); 57 (*t*-Bu, 100).

**Anal. Calcd for $C_{38}H_{61}GePTe$:** C, 60.93; H, 8.21. Found: C, 61.05; H, 8.41.

**Crystal Data for 3 and 4.** All data were collected at low temperatures using an oil-coated shock-cooled crystal on a Bruker-AXS APEX II diffractometer with Mo Kα radiation ($\lambda$ = 0.71073 Å). The structures were solved by direct methods[13] and all non hydrogen atoms were refined anisotropically using the least-squares method on $F^2$(Table 1).[14]

**Acknowledgment.** We acknowledge the Centre National de la Recherche Scientifique (contract CNRS/JSPS PRC 450), the Agence Nationale pour la Recherche (contract ANR-08-BLAN-0115-01), and the PHC Volubilis (MA/05/123) for financial support.

**Supporting Information Available:** X-ray crystallographic files in CIF format for **3** and **4**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM801133H

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[13] SHELXS-97: Sheldrick, G. M. *Acta Crystallogr.* **1990**, *A46*, 467.

[14] Sheldrick, G. M. *SHELXL-97, Program for Crystal Structure Refinement*; University of Göttingen: Göttingen, 1997.