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Comparison of reactivity of phosphagermaallene Tip(*t*-Bu)Ge=C=PMes* towards sulfur ylides

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ABSTRACT

Phosphagermaallene **1**, Tip(*t*-Bu)Ge=C=PMes* (Tip = 2,4,6-triisopropylphenyl, Mes* = 2,4,6-tri-*tert*-butylphenyl), reacts with diphenylsulfoniumylide ($Ph_2S{=}CH_2$) leading to adduct **2**, through a nucleophilic attack of the negatively charged carbon atom of the ylide on the positively charged germanium atom followed by a migration of one of the phenyl groups. By contrast, dimethyloxosulfoniummethylide ($Me_2S(O){=}CH_2$) appears much less reactive towards **1**: it preferentially undergoes an in-situ oxidation of THF leading to a γ-butyrolactone intermediate which gives a [2+2] cycloaddition by the C=O group with the Ge=C double bond to form **3**. The new compounds **2** and **3** were completely characterized by multinuclear NMR spectroscopy and by single crystal X-ray structural analysis.

1. Introduction

In the last three decades, a new research field about low coordinated compounds containing one or two elements of Groups 14 and 15 was developed [1–10]. It began with the synthesis of the first stable diphosphene Mes*P=PMes* (Mes* = 2,4,6-tri-*tert*-butylphenyl) by Yoshifuji [11], disilene $Mes_2Si{=}SiMes_2$ by West [12] and silene $(Me_3Si)_2Si{=}C(OSiMe_3)Ad$ by Brook [13] in 1981. Besides the study of such highly reactive double bonded alkene analogs, compounds containing two cumulative double bonds of the type E=C=E′ (E, E′ = group 14, 15) became also the focus of recent researches [14–20]. Among such cumulenic systems, the most intensively studied are phosphaheteroallenes P=C=E (E = Si, Ge) presenting two different double bonds and multiple reaction centers. In the case of phosphasilaallenes −P=C=Si<, only a transient system was evidenced [21] and in the case of tin, no such a system is known up to now. Besides the transient phosphagermaallene $Mes_2Ge{=}C{=}PMes^*$ [22], the first stable phosphagermaallene Tip(*t*-Bu)Ge=C=PMes* (**1**) (Tip = 2,4,6-triisopropylphenyl) was obtained in 2002 [23]. The reactivity of phosphagermaallene **1** has been extensively studied in the last decade. Most of the reactions occur on the Ge=C double bond which appears much more reactive than the P=C double bond. Various types of cycloadditions were observed: [2+1] with chalcogens [24], and [2+2] and [2+4] with various types of carbonyl derivatives [25–28] and multiply bonded nitrogen compounds [29], [2+3] with nitrones and nitrile oxides [29]. However, in some cases, (dimethyl acetylenedicarboxylate [30], diphenylketene [31], carbon disulfide and phenylisothiocyanate [26], benzonitrile [29], methylacrylate [25]) the phosphagermaallene **1** shows an unprecedented 1,3-dipole behavior that involves the whole Ge=C=P unit leading by a [3+2] cycloaddition with various double or triple bonds to new types of carbenes, the phosphagerma heterocyclic carbenes, analogs of the well-known N-heterocyclic carbenes (NHC). Ene reactions have also been evidenced in some cases [27,29]. In conclusion, phosphagermaallene **1** shows a great versatility in reactivity.

In this context we were curious to study the reactivity of **1** towards other dipolar compounds such as ylides. It has been shown that ylides react with double bond containing systems of type E=C

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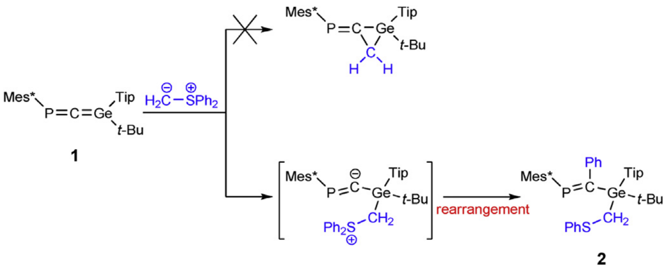
(E = C, N, O, S,...) leading to three-membered heterocyclic compounds [32–36]. The present study is focused on the reactivity study of phosphagermaallene **1**, Tip(*t*-Bu)Ge=C=PMes* (Tip = 2,4,6-triisopropylphenyl, Mes* = 2,4,6-tri-*tert*-butylphenyl), toward diphenylsulfoniumylide ($Ph_2S{=}CH_2$) and dimethyloxosulfoniummethylide ($Me_2S(O){=}CH_2$), respectively.

2. Results and discussion

Diphenylsulfoniumylide has been obtained in-situ by deprotonation of the methyldiphenylsulfoniumtriflate with *n*-BuLi in THF at low temperature [37]. The addition of one equivalent of phosphagermaallene **1** in Et_2O at −80 °C led to the formation of a unique compound as proved by the ^{31}P NMR spectrum of the reaction mixture (277.1 ppm). After evaporation of the solvents and crystallization from pentane, compound **2** (Mes*P=C(Ph)–Ge(*t*-Bu)(Tip)(CH_2SPh)) was isolated as colorless crystals in a good yield (70%). The low-field chemical shift of the phosphorus atom indicates that the P=C double bond was still present [38] and that only the Ge=C double bond was involved in the reaction. Moreover, in the ^{13}C NMR spectrum, a low-field shift of the carbon atom bonded to the phosphorus was observed (185.24 ppm, $^1J_{CP} = 88.1$ Hz), which is in good agreement with the presence of the P=C unsaturation. In the ^1H and ^{13}C NMR spectra, the most important point to be mentioned is the presence of a singlet at 3.15 ppm (^1H NMR) and a doublet at 27.69 ppm ($^3J_{CP} = 8.3$ Hz) (^{13}C NMR), respectively, corresponding to the CH_2S group. A free rotation of the Tip group was observed in the ^1H NMR spectrum as proved by the equivalence of the two ^{i}Pr groups; however, two doublets were observed for the diastereotopic Me groups of these ^{i}Pr groups. Compound **2** was unambiguously characterized by a single crystal X-ray structure analysis which confirms the addition of the ylide on the Ge=C bond with a transfer of one phenyl group to the carbon atom (see Fig. 1).

Thus, although the sulfur ylides have been reported as potential precursor of carbenes [39–42], the cycloaddition of the transient carbene on the Ge=C double bond to give a germirane has not been observed (Scheme 1).



Scheme 1. Synthesis of compound **2**.

The molecular structure of compound **2** is shown in Fig. 1. The germanium atom is in a slightly distorted tetrahedral geometry. The carbon atom of the P=C double bond is almost planar (sum of angles: 359.8°) and the Ge–C bond lengths (1.990(2) to 2.033(2) Å) lie at the upper limit for the Ge–C single bond (2.00 Å) [43], due to the large steric hindrance. The torsion angles (C34–P1–C1–Ge1 = 176° and C34–P1C1–C2 = 1.8°) involving the P=C double bond are in good agreement with a planar classical double bonded system.

In sharp contrast, the reaction of the dimethyloxosulfonium ylide (obtained by deprotonation of the trimethylsulfoxonium iodide with NaH in THF [36]) with **1** was more complex. The ^{31}P NMR spectrum of the crude mixture revealed the presence of several products including a major signal at 263 ppm. A slow crystallization in pentane at −30 °C allowed isolation of the corresponding compound in a low yield. The X-ray structure analysis proved the unexpected formation of the spiro-compound **3** which corresponds to the cycloadduct between the phosphagermaallene **1** and γ-butyrolactone (see Fig. 2). The latter was formed in-situ by the oxidation of THF.

THF is routinely used as solvent in the formation and the reactions of such kind of organometallic compounds and is considered as an inert solvent in this case. However, it is known that sometimes it can display some reactivity: strong organolithium bases can extract a proton from THF, usually initiating one or two ring fragmentation reactions [44]. Moreover, some oxidative reactions of THF leading to γ-butyrolactone have been reported, for

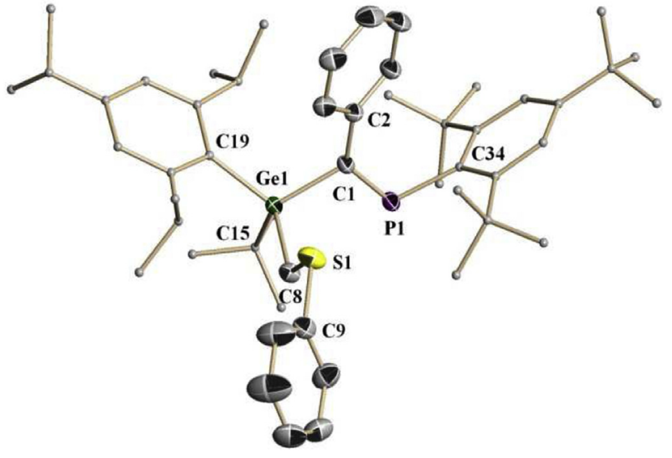


Fig. 1. Solid state structure of **2**. Thermal ellipsoids are drawn at the 50% probability level. Tip, Mes* and *t*-Bu groups have been simplified, hydrogen atoms and disorders have been omitted for clarity. Selected bond lengths (Å) and angles (°): Ge1–C1 1.990(2), Ge1–C8 1.984(2), Ge1–C15 2.033(2), Ge1–C19 2.002(2), C8–S1 1.808(2), S1–C9 1.778(2), C1–C2 1.481(2), C1–P1 1.682(2), P1–C34 1.851(2), C1–Ge1–C8 102.04(6), C1–Ge1–C15 115.44(6), C1–Ge1–C19 113.85(6), C8–Ge1–C15 100.21(6), C8–Ge1–C19 118.93(7), C15–Ge1–C19 106.02(7), Ge1–C1–P1 108.78(7), Ge1–C1–C2 120.48(10), C2–C1–P1 130.52(11), C1–P1–C34 110.01(7), Ge1–C8–S1 117.66(8), C8–S1–C9 99.84(7).

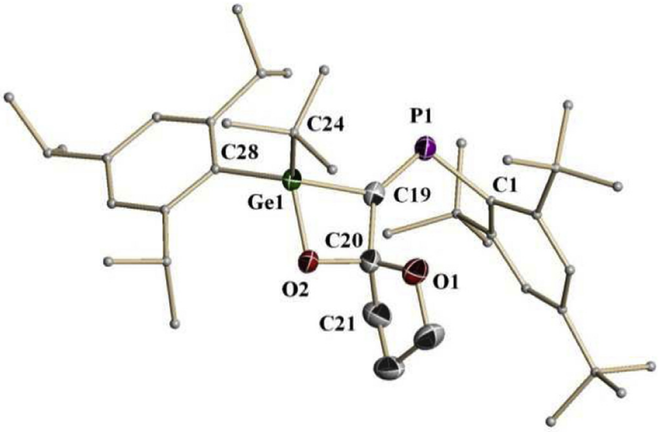


Fig. 2. Solid state structure of **3**. Thermal ellipsoids are drawn at the 50% probability level. Tip, Mes* and *t*-Bu groups have been simplified and hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°): Ge1–C19 1.964(3), Ge1–O2 1.835(2), Ge1–C24 1.986(4), Ge1–C28 1.959(3), P1–C19 1.650(4), P1–C1 1.845(3), C19–C20 1.545(5), C20–O2 1.453(4), C1–P1–C19 103.24, P1–C19–Ge1 133.44, Ge1–O2–C20 95.79, C19–C20–O2 101.12, O1–C20–O2 108.37, C1–P1–C19–Ge1 177.52, P1–C19–Ge1–C28 77.33.

example using calcium hypochlorite [45], zinc dichromate [46] and zinc permanganate [47]. In order to verify the hypothesis that **3** was formed by a reaction between **1** and γ-butyrolactone, trimethylsulfoxonium iodide was reacted with NaH in THF under described conditions and then the reaction mixture was stirred at room temperature for two additional hours. After filtration and distillation, γ-butyrolactone was isolated in low yield. Furthermore, the direct reaction of phosphagermaallene and the lactone was carried out. Treatment of **1** with a slight excess of lactone in diethyl ether at −80 °C yielded as expected the desired cycloadduct **3** as colorless crystals in a moderate yield (49%) (Scheme 2).

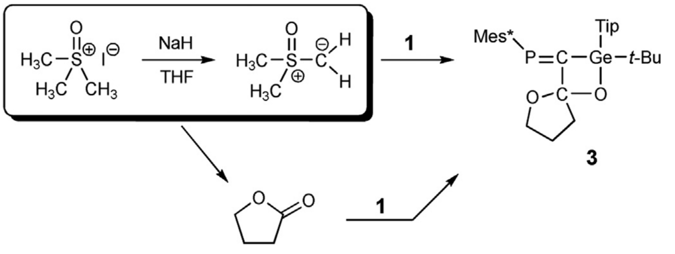
The ^{31}P NMR spectrum displayed, like in compound **2**, the formation of a sole compound with the chemical shift at 263.4 ppm proving that the [2 + 2] cycloaddition between the Ge=C and C=O double bonds occurred in this case. The presence of non-equivalent OCH_2 groups in the ^{1}H NMR spectrum at 3.11 and 3.84 ppm was in good agreement with such a bi-cyclic structure. However, this cycloadduct was unstable in solution and the ^{13}C NMR analysis could not be performed. It rapidly led to the formation of a new derivative which could not be identified. The reaction of dimethyloxosulfoniummethylide with **1** in other solvents like $CHCl_3$ and CH_2Cl_2 was not possible due to the instability of **1** in this environment.

The formation of the cycloadduct **3** was confirmed by a single crystal X-ray structural analysis.

The four-membered cycle Ge1–O2–C20–C19 is almost planar, with the germanium atom slightly outside of the four-membered cycle (the distance between the germanium atom and the plane O2, C20 and C19 is 0.017 Å and the angle between the planes O2, C20, C19 and O2, Ge1, C19 is only 4.39°. The C=P double bond is located in the same plane as O2, C20 and C19 atoms. The five-membered cycle is distorted with the C21 carbon atom at 0.599 Å of the mean plane constituted by the other four atoms; the angle between the plane containing the C20, C21, C22 atoms and the plane containing C20, C22, C23, and O1 atoms is 38.72°. The Ge-O2 bond length (1.834(2) Å) is comparable to that measured in germaoxetanes (1.826(2) Å [23]. Otherwise, the bond lengths and angles are comparable to those reported in the literature [43]. Only the *E* isomer relative to the P=C double bond was formed.

3. Conclusions

The reactivity of phosphagermaallene **1** towards sulfur containing ylides has been studied. With diphenylsulfoniumylide, a nucleophilic attack of the negatively charged carbon atom of the ylide on the positively charged germanium atom, followed by a migration of one of the phenyl group, led exclusively to acyclic adduct **2**. A three-membered germanium compound, which could be expected, was not formed. In the case of the dimethyloxosulfonium ylide, among a complex mixture, the cycloadduct **3** was surprisingly obtained as main product. This reaction can only be explained by a [2+2] cycloaddition between the Ge=C unsaturation and the C=O double bond of a γ-butyrolactone formed by oxidation of THF by the ylide. Thus, whereas diphenylsulfoniumylide reacts rapidly with **1** without formation of side products, dimethyloxosulfonium ylide reacts faster with the solvent.



Scheme 2. Synthesis of the cycloadduct **3**.

4. Experimental section

4.1. General

All manipulations were performed in a dry and oxygen-free atmosphere of argon by using standard Schlenk-line and glove box techniques. Solvents were purified with the MBRAUN SBS-800 purification system. NMR spectra were recorded with a Bruker Avance II 300 apparatus: ^{1}H (300.13 MHz), ^{13}C (75.48 MHz), ^{31}P (121.50 MHz). Chemical shifts are expressed in parts per million with residual solvent signals as internal reference (^{1}H and ^{13}C{^{1}H}) or with an external reference (H_3PO_4 for ^{31}P). In the case of the new compounds, the assignments of ^{1}H signals together with those in ^{13}C NMR spectra were obtained from 2D heteronuclear experiments (HSQC and HMBC). Melting points were measured in a sealed capillary using the Stuart automatic melting point SMP40 apparatus. The phosphagermaallene **1** [23] and the methyldiphenylsulfoniumtriflate [48] were prepared according to literature procedures. The phosphagermaallene **1** could be prepared in-situ or kept in a glove box in solid form. Trimethylsulfoxonium iodide $Me_3S(O)I$ was purchased from Aldrich and used without further purification.

4.2. Acyclic compound (**2**)

To a solution of $Ph_2(Me)SOTf$ (182 mg, 0.519 mmol) in THF (2 mL), a solution of *n*-BuLi 1.6 M in 0.34 mL, 0.545 mmol was added dropwise at −80 °C. The mixture in hexane (0.34 mL, 0.545 mmol) was stirred for 20 min at this temperature. The formed ylide was used without isolation and further purification. The phosphagermaallene **1** was prepared from the previously formed Tip(*t*-Bu)(F)Ge–C(Cl)=PMes*(350 mg, 0.518 mmol) in diethyl ether (3 mL) by adding a solution of *t*-BuLi 1.7 M in pentane (0.32 mL, 0.544 mmol) at −80 °C. After stirring for 30 min at this temperature, the red reaction mixture was allowed to warm up to room temperature to get phosphagermaallene **1** from the previously formed Tip(*t*-Bu)(F)Ge–C(Li)=PMes* and became red–brown; after 10 min, it was cooled again to −80 °C and the solution containing the ylide was slowly added. The cooling bath was removed after 10 min and the solution was allowed to warm up to room temperature, while its color became brownish red. The solvents were evaporated under low pressure and replaced by pentane. The mixture was filtered to eliminate LiF. Compound **2** was crystallized from pentane (0.3 g, 0.364 mmol, yield 70%), m.p.: 177–178 °C.

^{1}H NMR ($CDCl_3$) $\delta = 0.71$ (broad s, 6H, *o*-CH*Me*Me′, Tip), 1.17 (d, $^3J_{HH} = 6.9$ Hz, 6H, *p*-CH*Me*$_2$, Tip), 1.18 (d, $^3J_{HH} = 6.6$ Hz, 6H, *o*-CHMe*Me*′, Tip), 1.23 (s, 9H, *o*-C*Me*$_3$, Mes*), 1.36 (s, 9H, *p*-C*Me*$_3$, Mes*), 1.50 (s, 9H, Ge–C*Me*$_3$), 1.70 (s, 9H, *o*-C*Me*$_3$, Mes*), 2.77 (sept, $^3J_{HH} = 6.9$ Hz, 1H, *p*-C*H*Me$_2$, Tip), 3.10 (sept, $^3J_{HH} = 6.6$ Hz, 2H, *o*-C*H*MeMe′, Tip), 3.15 (s, 2H, C*H*$_2$–S), 6.23 (d, $^3J_{HH} = 7.8$ Hz, 2H, *o*-C*H*, Ph–C), 6.58 (t, $^3J_{HH} = 7.8$ Hz, 2H, *m*-C*H*, Ph–C), 6.70–6.77 (m, 1H, *p*-C*H*, Ph–C), 6.85 (s, 2H, *m*-C*H*, Tip), 7.09–7.14 (m, 1H, *p*-C*H*, Ph–S), 7.24–7.34 (m, 5H, *o*- and *m*-C*H*, Ph–S, *m*-C*H*, Mes*), 7.43 (s, 1H, *m*-C*H*, Mes*).

^{13}C NMR ($CDCl_3$) $\delta = 23.74$ and 23.83 (2s, *p*-CH*MeMe*′, Tip), 25.14 and 26.87 (2s, *o*-CH*MeMe*′, Tip), 27.69 (d, $^3J_{CP} = 8.3$ Hz, CH$_2$–S), 30.32 (s, Ge–C*Me*$_3$), 31.47 (s, *p*-C*Me*$_3$, Mes*), 32.67 and 32.79 (2s, *o*-C*Me*$_3$, Mes*), 33.76 (s, *p*-CHMeMe′, Tip), 34.42 (s, *o*-CHMeMe′, Tip), 34.97 (s, *p*-CMe$_3$, Mes*), 37.96 (d, $^3J_{CP} = 0.8$ Hz, *o*-CMe$_3$, Mes*), 38.06

(s, *o*-CMe_3, Mes*), 121.12 and 123.30 (2s, *m*-CH, Mes*), 121.74 (s, *m*-CH, Tip), 124.61 (s, *p*-CH, Ph–S) 126.08 (d, $^5J_{CP} = 3.6$ Hz, *p*-CH, Ph–C), 126.48 and 128.60 (2s, *o*-CH and *m*-CH, Ph–S), 126.62 (d, $^4J_{CP} = 1.7$ Hz, *m*-CH, Ph–C), 129.17 (d, $^3J_{CP} = 11.1$ Hz, *o*-CH, Ph–C), 132.29 (d, $^3J_{CP} = 13.2$ Hz, *ipso*-C, Tip), 138.09 (d, $^1J_{CP} = 82.8$ Hz, *ipso*-C, Mes*), 141.17 (d, $^2J_{CP} = 17.9$ Hz, *ipso*-C, Ph–C), 141.69 (s, *ipso*-C, Ph–S), 148.98 (s, *p*-C, Tip), 150.44 and 153.58 (2s, *o*-C, Mes*), 154.10 (d, $^4J_{CP} = 4.0$ Hz, *p*-C, Mes*), 154.58 (s, *o*-C, Tip), 185.24 (d, $^1J_{CP} = 88.1$ Hz, P=C=Ge).

^{31}P NMR ($CDCl_3$) $\delta = 277.1$ ppm.

4.3. Cycloadduct (**3**)

4.3.1. Starting from the sulfoxonium ylide

To a solution of sodium hydride (21 mg, 0.88 mmol, 60% dispersion in mineral oil washed with pentane) in THF (3 mL), trimethylsulfoxonium iodide (88 mg, 0.4 mmol) was added at 0 °C. At this mixture, after stirring 5 min, a solution of Tip(*t*-Bu)Ge=C=PMes* **1** (250 mg, 0.4 mmol) in diethyl ether (3 mL) was added at 0 °C. The mixture was allowed to warm up to room temperature and all solvents were evaporated under reduced pressure. According to the ^{31}P NMR studies, compound **3** was formed in low yield (15–20%). The crystals of this cycloadduct **3** were obtained from pentane.

4.3.2. Starting from the γ-butyrolactone

The phosphagermaallene **1** was prepared as previously described from a solution 1.7 M of *t*-BuLi (0.457 mL, 0.777 mmol) in pentane to a solution of Tip(*t*-Bu)(F)Ge–C(Cl)=PMes*(0.5 g, 0.74 mmol) in diethyl ether (6 mL) at −90 °C. To the solution of **1** cooled at −80 °C, freshly distilled γ-butyrolactone (0.12 g, 1.394 mmol) was added dropwise. After 15 min a yellow precipitate was formed. All solvents were evaporated under low pressure and pentane (18 mL) was added; the reaction mixture was then filtered and concentrated. After 12 h at −24 °C, compound **3** was isolated as a pale yellow powder (0.26 g, 0.367 mmol, yield 49%).

^{1}H NMR (C_6D_6) 1.14 (d, $^3J_{HH} = 6.9$ Hz, 3H, CHMe*Me*′, Tip), 1.15 (d, $^3J_{HH} = 6.9$ Hz, 3H, CHMe*Me*′, Tip), 1.32 (d, $^3J_{HH} = 6.6$ Hz, 3H, CHMe*Me*′, Tip), 1.41 (d, $^3J_{HH} = 6.6$ Hz, 3H, CHMe*Me*′, Tip), 1.49 (d, $^3J_{HH} = 6.3$ Hz, 3H, CHMe*Me*′, Tip), 1.54 (d, $^3J_{HH} = 6.9$ Hz, 3H, CHMe*Me*′, Tip), 1.24, 1.44, 1.53 and 1.71 (4s, 4 × 9H, C*Me*$_3$ of Mes* and Ge–C*Me*$_3$), 1.50–1.96 (m, 2× 2H, CH_2), 2.73 (sept, $^3J_{HH} = 6.9$ Hz, 1H, *p*-C*H*MeMe′, Tip), 3.06–3.15 (m, 1H, OCH*H*′), 3.26 (sept, $^3J_{HH} = 6.6$ Hz, 2H, *o*-C*H*MeMe′, Tip), 3.80–3.90 (m, 1H, OC*H*H′), 7.18 (s, 2H, *m*-C*H*, Tip), 7.27 and 7.43 (2s, 2× 1H, *m*-C*H*, Mes*).

^{31}P NMR (C_6D_6) $\delta = 263.4$ ppm.

MS-HR Calcd for $C_{42}H_{66}GeO_2P$: 707.4012. Found: 707.4024.

4.4. X-ray crystallography

X-ray data for compound **2** were collected at low temperature (193 K) on a Bruker-AXS SMART APEX II diffractometer, and for compound **3** on a Bruker-AXS APEX II Quazar diffractometer using a 30 W air-cooled microfocus source (ImS) with focusing multilayer optics with graphite-monochromated MoK alpha radiation (wavelength = 0.71073 Å) by using phi- and omega-scans. The data were integrated with SAINT, and an empirical absorption correction with SADABS was applied [49,50]. The structures were solved by direct methods, using SHELXS-97 [51] and refined using the least-squares method on F^2 [52]. All non-H atoms were treated anisotropically. The H atoms were located by difference Fourier maps and refined with a riding model. Crystallographic data are summarized in Table 1.

Table 1
Selected crystallographic data and collection parameters.

	2	**3**
Formula	$C_{51}H_{73}GePS$	$C_{42}H_{67}GeO_2P$
fw	821.71	707.54
Temp (K)	180(2)	193(2)
Wavelength (Å)	0.71073	0.71073
Crystal system	Triclinic	Monoclinic
Space group	$P\bar{1}$	$P2_1/n$
a (Å)	9.9717(4)	10.135(2)
b (Å)	15.5744(7)	16.120(4)
c (Å)	15.9957(7)	25.137(5)
α (°)	105.247(2)	–
β (°)	100.413(2)	94.175(12)
γ (°)	93.703(2)	–
V [Å^3]	2340.76(17)	4095.9(15)(3)
Z	2	4
d_{calcd} (Mg m^{-3})	1.166	1.147
μ (mm^{-1})	0.765	0.818
F(000)	884	1528
Crystal size [mm^{-1}]	0.40 × 0.20 × 0.20	0.08 × 0.04 × 0.04
θ range (°)	5.12–28.28	5.12–26.37
No of rflns collected	64,192	44,499
No of indep rflns	11,497 ($R_{int} = 0.0375$)	8307 ($R_{int} = 0.1346$)
GOF on F^2	1.018	0.988
*R*1, *wR*2 ($I > 2\sigma(I)$)	0.0320, 0.0731	0.0536, 0.1034
*R*1, *wR*2 (all data)	0.0458, 0.0790	0.1203, 0.1258

Acknowledgments

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Appendix A. Supplementary material

CCDC 952746 (**2**) and 952747 (**3**) contain the supplementary crystallographic data for this paper. This data can be obtained free of charge from The Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif.

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