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# Some addition reactions of bisgermavinylidene

**Wing-Por Leung*, Kwok-Wai Kan, Cheuk-Wai So and Thomas C. W. Mak**

Department of Chemistry, The Chinese University of Hong Kong, Shatin, New Territories, Hong Kong, People's Republic of China

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**The reaction of bisgermavinylidene $[(Me_3SiN{=}PPh_2)_2C{=}Ge{\rightarrow}Ge{=}C(PPh_2{=}NSiMe_3)_2]$ (1) with AdNCO (Ad = Adamantyl) afforded the [2 + 2] cycloadditon product $[(Me_3SiN{=}PPh_2)_2CGeC(O)NAd]$ (2). Similar reaction of 1 with $Ph_3SiOH$ in tetrahydrofuran (THF) yielded the base-stabilized germanium(II) triphenylsiloxide $[H_2C(PPh_2{=}NSiMe_3)_2Ge(OSiPh_3)_2]$ (3). The results suggested that reactive germavinylidene may exist in solution and is capable of forming addition reaction products. The X-ray structures of 2 and 3 were determined. Copyright © 2007 John Wiley & Sons, Ltd.**

**KEYWORDS:** germanium; germene; cycloaddition; germavinylidene

## INTRODUCTION

Germenes are compounds containing a double bond between tetravalent germanium and carbon (C=Ge). The chemistry has attracted much attention and has been the focus of several reviews.[1–7] The synthesis and isolation of germenes was found to be difficult because of their great tendency to undergo dimerization. Nevertheless, germenes $R_2Ge{=}CR'_2$ can be stabilized by incorporating sterically bulky substituents at both germanium and carbon.[8–10] For example, $Mes_2Ge{=}CR_2$ (Mes = 2,4,6-trimethylphenyl, $CR_2$ = fluorenylidene)[4] and $[(Me_3Si)_2Ge{=}C(BBu^t)_2C(SiMe_3)_2]$[8] have been reported and structurally characterized. The most common routes for the synthesis of germene are the addition–elimination reaction of *tert*-butyllithium with halovinyligermane and the germylene–carbene coupling reaction. The reactivities of germene such as 1,2-addition or $[2 + n]$ cycloadditon have been extensively studied.[11–14] In contrast, the low-valent germavinylidenes (>C=Ge) are scarcely found and had only been detected by laser-induced fluorescence spectroscopy.[15]

The unusual structure and the unknown reactivity of germavinylidenes have attracted our interest and we have reported the synthesis and structure of bisgermavinylidene $[(Me_3SiN{=}PPh_2)_2C{=}Ge \rightarrow Ge{=}C(PPh_2{=}NSiMe_3)_2]$ (**1**).[16] The existence of a monomeric germavinylidene intermediate in solution was demonstrated in the synthesis of manganese–germavinylidene complex $[(Me_3SiN{=}PPh_2)_2C{=}Ge \rightarrow Mn(CO)_2Cp]$ ($Cp = \eta^5$-$C_5H_5$).[17] We have also reported the synthesis of $[(Me_3SiN{=}PPh_2)_2\{(cod)RhCl\}CGeCl]$ (cod = 1,5-cyclooctadiene) from the 1,2-addition reaction of **1** with (cod)RhCl.[17]

We anticipated that bisgermvinylidene **1** is a potential source of reactive monomeric germavinylidene 'Ge=$C(PPh_2{=}NSiMe_3)_2$' intermediate by breaking the weak Ge–Ge interaction of **1** in solution. In this paper, we report the [2 + 2] cycloaddition reaction of germavinylidene with AdNCO (Ad = Adamantyl) showing the existence of the carbon–germanium double bond character in **1**. The synthesis of base-stabilized germanium(II) triphenylsiloxide which is believed to form from the 1,2-addtion reaction of germavinylidene with $Ph_3SiOH$ is also reported.

## RESULTS AND DISCUSSION

### Synthesis of $[(Me_3SiN{=}PPh_2)_2CGeN(Ad)C{=}O]$ (2)

Treatment of bisgermavinylidene **1** with two equivalents of AdNCO (Ad = Adamantyl) in THF afforded the [2 + 2] cycloaddition adduct $[(Me_3SiN{=}PPh_2)_2CGeN(Ad)C{=}O]$ (**2**) (Scheme 1). The X-ray structure of **2** shows that the Ge–C bond distance increases as the bond order is reduced from two to one by the cycloaddition reaction, which supports that the existence of the Ge=C bond in **1**. Similar results have been found in the [2 + 2] cycloaddition reactions of $[MCl_2\{C(PPh_2{=}NSiMe_3)_2$-$\kappa C, \kappa^2 N, N'\}]$ (M = Zr, Hf) with heteroallenes.[18–20]

*Correspondence to: Wing-Por Leung, Department of Chemistry, The Chinese University of Hong Kong, Shatin, New Territories, Hong Kong, People's Republic of China.
E-mail: kevinleung@cuhk.edu.hk
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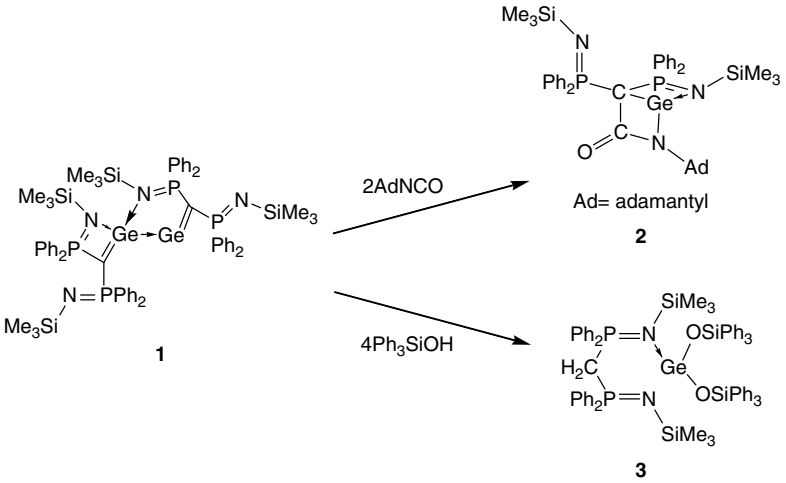
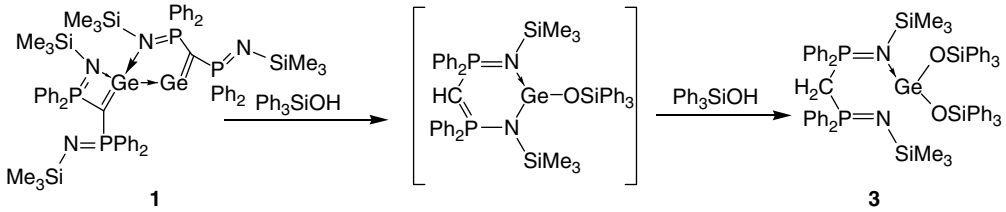



**Scheme 1.** .




**Scheme 2.** .

*Synthesis of [$H_2C(PPh_2{=}NSiMe_3)_2Ge(OSiPh_3)_2$] (**3**)*
The reaction of bisgermavinylidene **1** with four equivalents of $Ph_3SiOH$ in THF yielded germanium(II) triphenylsiloxide imine complex [$H_2C(PPh_2{=}NSiMe_3)_2Ge(OSiPh_3)_2$] (**3**) (Scheme 1). It is proposed that the $Ph_3SiOH$ reacted with germavinylidene to give the 1,2-addition intermediate [$HC(PPh_2{=}NSiMe_3)_2GeOSiPh_3$], followed by further protonation at the methanide carbon by $Ph_3SiOH$ to yield **3** (Scheme 2). Attempts to isolate the intermediate [$HC(PPh_2{=}NSiMe_3)_2GeOSiPh_3$] by changing the amount of $Ph_3SiOH$ added in the reaction was unsuccessful. Similar Group 14 metal siloxides have been prepared by the reaction of $Ph_3SiOH$ with [{$M(OBu^t)_2$}$_n$] (M = Ge, Sn).[21]

## Spectroscopic properties

Compounds **2** and **3** were isolated as colorless crystalline solids. They are air-sensitive, soluble in THF and sparingly soluble in $Et_2O$. They were characterized by NMR spectroscopy and X-ray structure analysis.

The $^1H$ and $^{13}C$ NMR spectra of **2** displayed one set of resonances for the bis(iminophosphorano)methanediide ligand and adamanyl group. The $^{31}P$ NMR spectrum of **2** showed one sharp singlet at $\delta$ 25.08 ppm which is not consistent with the X-ray structure. This may be due to the fluxional behavior of imino nitrogen atoms at the germanium center in solution.

The $^1H$ NMR spectrum of **3** showed a quartet at $\delta$ 3.63 ppm ($J_{H-P}$ = 15 Hz) assigned to the two methylene protons with coupling to two different phosphorus nuclei. The proton-decoupled $^{31}P$ NMR spectrum displayed two doublets at $\delta$ 21.89–22.01 ($J_{P-P}$ = 36 Hz) and $\delta$ 32.46–32.58 ppm ($J_{P-P}$ = 36 Hz), consistent with the solid-state structure. The $^{13}C$ NMR spectrum is normal.

## X-ray structures

The molecular structures with the atom-numbering schemes for **2** and **3** are shown in Figs 1 and 2, respectively. Selected bond distances (Å) and angles (deg) of **2** and **3** are listed in Tables 1 and 2, respectively.

Compound **2** comprises a four-membered C(1)–C(51)–N(3)–Ge(1) ring which is almost planar (sum of angles = 358.7°). The germanium center displays a trigonal–pyramidal geometry as indicated by the sum of angles of 242.17° at Ge(1), consistent with a stereoactive lone pair at the germanium center. The Ge(1)–C(1) bond distance of 2.135(4) Å in **2** is similar to the Ge–C single bond distance of 2.135(4) Å in Ge[$CPh(SiMe_3)(C_5H_4N$-2)]$_2$[22] and 2.076(1) Å in [$(Me_3SiN{=}PPh_2)_2${(cod)Rh}CGeCl],[17] but longer than the Ge=C distances of 1.905(8) and 1.908(7) Å in **1**,[16] showing that the bond order of the Ge–C bond changed from two to one. The Ge(1)–N(3) bond distance of 1.973(3) Å in **2** is similar to those found in $ArGeN(SiMe_3)_2$ [Ar =



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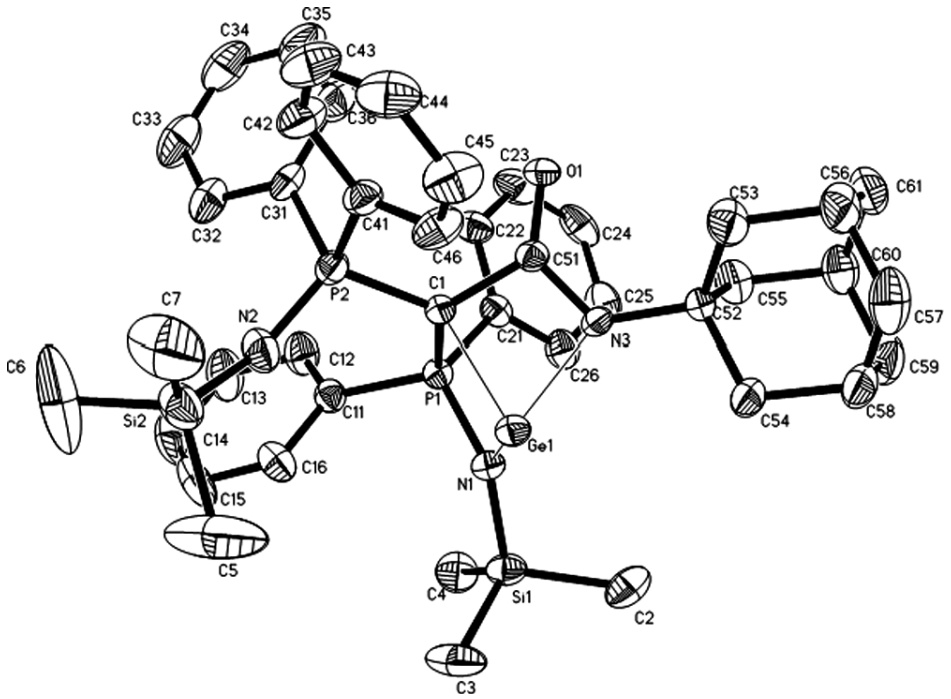


**Figure 1.** Molecular structure of **2**. Hydrogen atoms are omitted for clarity (30% probability ellipsoids).

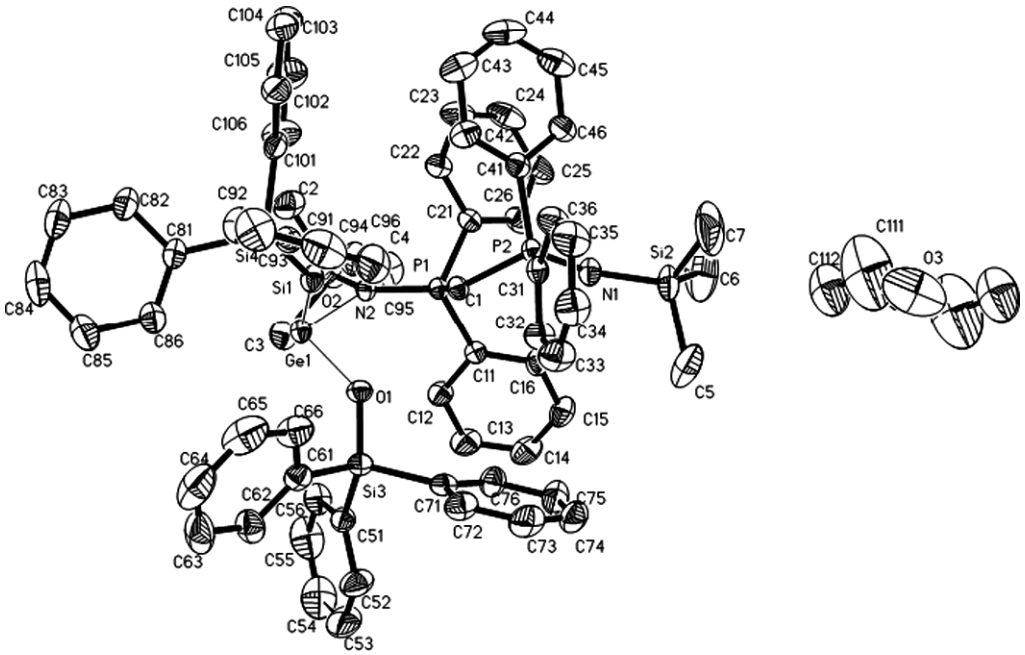


**Figure 2.** Molecular structure of **3**. Hydrogen atoms are omitted for clarity (30% probability ellipsoids).

2,6-bis((diethylamino)methyl)phenyl] [1.956(0) Å][23] and [Ge{C($C_5H_4$N-2)C(Ph)N($SiMe_3$)$_2$}{N($SiMe_3$)C(Ph)($SiMe_3$)($C_5H_4$N-2)}] [1.940(2) Å].[24] The Ge(1)–N(1) bond distance of 2.039(3) Å in **2** is similar to the reported intramolecular N → Ge bond distances.[25] The C(1)–C(51), C(51)–O(1) and C(51)–N(3) bond distances in **2** are normal.

Compound **3** comprises a germanium(II) bis(triphenylsiloxide) coordinated to the imino group of bis(iminophosphorano)methane. The angle sum at the germanium center is 285.1°, which deviates significantly from a $sp^3$ tetrahedral geometry, so germanium adopts a three-coordinate trigonal–pyramidal geometry. The Ge(1)–N(1) bond distance of



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**Table 1.** Selected bond distances (Å) and angles (deg) for compound **2**

| | | | |
|---|---|---|---|
| Ge(1)–N(3) | 1.973(3) | P(2)–N(2) | 1.535(4) |
| Ge(1)–N(1) | 2.039(3) | P(2)–C(1) | 1.798(4) |
| Ge(1)–C(1) | 2.135(4) | N(3)–C(51) | 1.347(5) |
| P(1)–N(1) | 1.607(3) | N(3)–C(52) | 1.478(5) |
| P(1)–C(1) | 1.801(4) | C(1)–C(51) | 1.529(6) |
| N(3)–Ge(1)–N(1) | 97.4(1) | C(51)–N(3)–Ge(1) | 95.5(2) |
| N(3)–Ge(1)–C(1) | 67.2(1) | C(52)–N(3)–Ge(1) | 134.4(2) |
| N(1)–Ge(1)–C(1) | 77.6(1) | C(51)–C(1)–P(2) | 121.8(3) |
| N(1)–P(1)–C(1) | 100.1(2) | C(51)–C(1)–P(1) | 110.1(3) |
| N(2)–P(2)–C(1) | 111.3(2) | P(1)–C(1)–P(2) | 120.9(2) |
| P(1)–N(1)–Ge(1) | 99.6(3) | C(51)–C(1)–Ge(1) | 87.4(2) |
| N(3)–C(51)–C(1) | 104.5(3) | P(1)–C(1)–Ge(1) | 86.8(2) |

**Table 2.** Selected bond distances (Å) and angles (deg) for compound **3**

| | | | |
|---|---|---|---|
| Ge(1)–O(1) | 1.852(2) | P(1)–C(1) | 1.822(3) |
| Ge(1)–O(2) | 1.865(2) | P(2)–N(1) | 1.536(3) |
| Ge(1)–N(2) | 2.114(2) | P(2)–C(1) | 1.820(3) |
| P(1)–N(2) | 1.603(2) | | |
| O(1)–Ge(1)–O(2) | 95.7(9) | Si(3)–O(1)–Ge(1) | 138.2(1) |
| O(1)–Ge(1)–N(2) | 91.6(9) | Si(4)–O(2)–Ge(1) | 136.2(1) |
| O(2)–Ge(1)–N(2) | 97.8(9) | P(2)–C(1)–P(1) | 120.9(2) |

Symmetry transformations used to generate equivalent atoms: $-x+2, -y+3, -z+1$.

2.114(2) Å in **3** is similar to the N → Ge bond distances found in MamxGeOEt (Mamx = methylaminomethyl-*m*-xylyl) [2.123 (3) Å][26] and [ArGe(OH){W(CO)$_5$}] (Ar = 2,6-bis((diethylamino)methyl)phenyl) [2.113(3)Å].[10] The Ge–O bond distance [1.852(2) Å, 1.865(2)] in **3** is slightly longer than some reported Ge–O bond distances [1.817–1.829 Å],[27,28] indicating a considerable p$\pi$–d$\pi$ back donation from the oxygen to germanium atom. The Ge–O–Si bond angles of 138.2(1)° and 136.2(1)° in **3** are comparable to that of 150.2(2)° in [{Ge($\mu$-OBu$^t$)(OSiPh$_3$)}$_2$].[21] It is suggested that the ligand steric repulsion in **3** decreases the Ge–O–Si angles. The bond distances of the ligand backbone are similar to bis(iminophosphorano)methane [(Me$_3$SiN=PPh$_2$)$_2$CH$_2$] [P–N = 1.536(2)Å; C–P = 1.825(1) Å].[29]

## EXPERIMENTAL

### General procedures

All manipulations were carried out under an inert atmosphere of dinitrogen gas by standard Schlenk techniques. Solvents were dried over and distilled from $CaH_2$ (hexane) and/or Na ($Et_2O$, toluene and THF). Bisgermavinylidene [(Me$_3$SiN=PPh$_2$)$_2$C=Ge → Ge=C(PPh$_2$=NSiMe$_3$)$_2$] (**1**) was prepared using literature procedures.[16] AdNCO and Ph$_3$SiOH were purchased from Aldrich Chemicals and used without further purification. The $^1$H (300.13 MHz), $^{13}$C (75.47 MHz) and $^{31}$P (121.49 MHz) spectra were recorded on Brüker WM-300 spectrometer. The NMR spectra were recorded in THF-$d_8$ or Benzene-$d_6$ and the chemical shifts $\delta$ are relative to $SiMe_4$ and 85% $H_3PO_4$ for $^1$H, $^{13}$C and $^{31}$P, respectively.

### Reaction of 1 with AdNCO

A solution of **1** (0.66 g, 0.52 mmol) in THF (20 ml) was added slowly to the AdNCO (0.18 g, 1.04 mmol) in THF (20 ml) at 0 °C. The resultant colorless solution was raised to room temperature and stirred for 34 h. The volatiles were removed under reduced pressure. The residue was extracted with $Et_2O$. After filtration and concentration of the filtrate, **2** was obtained as colorless crystals. Yield: 0.48 g (57%); m.p. 123–125 °C. Anal. found: C, 61.89; H, 6.81; N, 5.23. Calcd for $C_{42}H_{53}GeN_3OP_2Si_2$: C, 62.54; H, 6.62; N, 5.21. $^1$H NMR (THF-$d_8$): $\delta = -0.09$ (s, 18H, $SiMe_3$), 1.60 (b.s, 6H, $CH_2$-Ad), 1.78 (b. dd, 6H, $CH_2$-Ad), 1.91 (b.s, 3H, CH-Ad), 7.05–7.33 (m, 8H, Ph), 7.38–7.52 (m, 4H, Ph), 7.56–7.64 (m, 4H, Ph), 7.68–7.90 (m, 4H, Ph). $^{13}$C{$^1$H} NMR (THF-$d_8$): $\delta = 3.58$ (s, $SiMe_3$), 31.13 (s, $CH_2$-Ad), 38.03 (s, $CH_2$-Ad), 43.17 (s, CH-Ad), 54.53 (s, quaternary C-Ad), 128.43, 128.60, 128.83, 128.99, 132.10, 132.50, 132.86, 133.00, 135.11, 135.30 (Ph). $^{31}$P{$^1$H} NMR (THF-$d_8$): $\delta = 25.08$.

### Reaction of 1 with Ph$_3$SiOH

A solution of **1** (0.60 g, 0.48 mmol) in THF (20 ml) was added slowly to the Ph$_3$SiOH (0.53 g, 1.91 mmol) in THF (20 ml) at 0 °C. The resultant colorless suspension was raised to room temperature and stirred for 30 h. The volatiles were removed under reduced pressure. The residue was extracted with $Et_2O$. After filtration and concentration of the filtrate, **3** was obtained as colorless crystals. Yield: 0.47 g (41%); m.p. 147–150 °C. Anal. found: C, 67.25; H, 6.27; N, 2.40. Calcd for $C_{67}H_{70}GeN_2O_2P_2Si_4.Et_2O$: C, 67.88; H, 6.42; N, 2.23. $^1$H NMR (Benzene-$d_6$): $\delta = 0.15$, (s, 9H, $SiMe_3$), 0.26 (s, 9H, $SiMe_3$), 3.58 (q, 2H, $PCH_2P$, $J_{H-P} = 15$ Hz), 7.20–7.29 (m, 20H, Ph), 7.34–7.39 (m, 10H, Ph), 7.58–7.66 (m, 10H, Ph), 7.69–7.73 (m, 10H, Ph). $^{13}$C{$^1$H} NMR (Benzene-$d_6$): $\delta = 1.19$ (s, $SiMe_3$), 3.97 (s, $SiMe_3$), 36.78 (PCP), 127.70, 128.03, 128.30, 128.46, 128.93, 129.62, 130.29, 130.29, 131.44, 131.58, 132.05, 132.19, 135.83, 136.24, 136.53, 137.86, 139.13, 140.54 (Ph). $^{31}$P{$^1$H} NMR (benzene-$d_6$): $\delta = 21.89–22.01$ (d, $J_{p-p} = 36$ Hz), 32.46–32.58 (d, $J_{p-p} = 36$ Hz).

### X-ray crystallography

Single crystals were sealed in Lindemann glass capillaries under nitrogen. X-ray data of **2** and **3** were collected at 293(2) K on a Rigaku R-AXIS II imaging plate using graphite-monochromatized Mo $K_\alpha$ radiation ($I$ = 0.71073 ´Å) from a rotating-anode generator operating at 50 kV and 90 mA. Crystal data for **2** ($C_{42}H_{53}GeN_3OP_2Si_2$): $M$ = 806.58, monoclinic, $P2_1/c$, $a = 21.181(2)$, $b = 10.2072(10)$, $c = 20.1526(19)$ ´Å, $\alpha = 90$, $\beta = 97.370(12)$, $\gamma = 90°$, $V$ =



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4321.0(7) ´Å$^3$, $Z = 4$, $R$ [10370 data with $I < 2\sigma(I)$; $\theta_{max}$ 28.00°] = 0.0535, $w$R (all 28 681 data) = 0.1382. Crystal data for **3** ($C_{67}H_{70}GeN_2O_2P_2Si_4.1/2Et_2O$): $M = 1219.20$, triclinic, P − 1, $a = 13.2690(15)$, $b = 13.6570(16)$, $c = 21.124(2)$ ´Å, $\alpha = 90.46(2)$, $\beta = 98.483(12)$, $\gamma = 118.222(2)°$, $V = 3325.0(7)$ ´Å$^3$, $Z = 2$, $R$ [15794 data with $I < 2\sigma(I)$; $\theta_{max}$28.06°] = 0.0521, $w$R (all 22 798 data) = 0.1257. The structures were solved by direct phase determination using SHELXTL-PC[30] on a PC 486 and refined by full-matrix least squares with anisotropic thermal parameters for the non-hydrogen atoms. Hydrogen atoms were introduced in their idealized positions and included in structure factor calculations with assigned isotropic temperature factor calculations. CCDC reference numbers CCDC 642508 and 642509 contain the supplementary crystallographic data for this paper.

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