

# Facile Access to a Stable Divalent Germanium Compound with a Terminal PH<sub>2</sub> Group and Related PR<sub>2</sub> Derivatives

Shenglai Yao,<sup>†</sup> Markus Brym,<sup>†</sup> Klaus Merz,<sup>‡</sup> and Matthias Driess<sup>\*†</sup>

Technische Universität Berlin, Institute of Chemistry: Metalorganics and Inorganic Materials, Sekr. C2, Strasse des 17. Juni 135, D-10623 Berlin, Germany, and Faculty of Chemistry, Ruhr-Universität Bochum, Universitätsstrasse 150, D-44801 Bochum, Germany

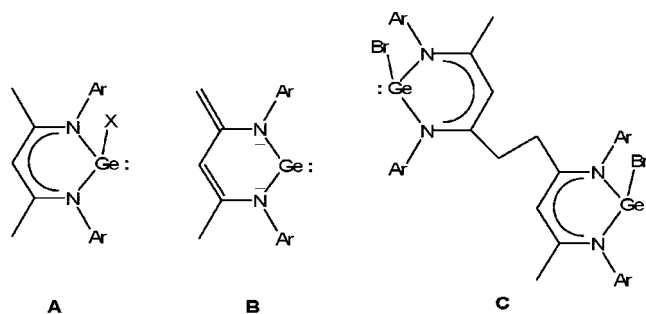
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The first stable  $\beta$ -diketiminate germanium(II) complexes LGeY [L = CH{(CMe)(2,6-*i*Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>N)}<sub>2</sub>] with terminal phosphanyl groups Y (Y = PH<sub>2</sub>, PHR, and PR<sub>2</sub>) are described. Thus, LGePH<sub>2</sub> (**2**) is synthesized by salt metathesis reaction of LGeCl (**1**) with lithium phosphanide and can be isolated in the form of orange crystals in 83% yield. Its silylation with 1 molar equiv of Me<sub>3</sub>SiOTf (OTf = OSO<sub>2</sub>CF<sub>3</sub>) in the presence of triethylamine as auxiliary base leads solely to LGeP(H)SiMe<sub>3</sub> (**3**). In contrast, reaction of **2** with 2 molar equiv of Me<sub>3</sub>SiOTf does not lead to the desired product LGeP(SiMe<sub>3</sub>)<sub>2</sub> (**4**), but LGeOTf (**6**) and HP(SiMe<sub>3</sub>)<sub>2</sub> are formed. However, compound **4** is conveniently accessible from **1** and the corresponding lithium phosphanide LiP(SiMe<sub>3</sub>)<sub>2</sub>. While attempts to metalate the PH<sub>2</sub> group in **2** applying BuLi and Me<sub>2</sub>Zn, respectively, lead merely to Ge–P fission and undesired side products, its conversion with <sup>187</sup>Bu<sub>2</sub>Hg occurs without Ge–P fission but P–P bond formation to give the novel *P,P'*-bis(phosphanylgermylene) LGeP(H)–P(H)GeL (**5**), elemental mercury, and isobutane. Compounds **2**–**6** have been fully characterized, including elemental analyses, NMR spectroscopy, and single-crystal X-ray diffraction analysis.

## Introduction

Due to their carbene-like properties, molecular divalent germanium species (germylenes) have attracted much attention in the past decades. Since the seminal work by Lappert et al. on the synthesis of isolable germylenes in 1976,<sup>1</sup> remarkable progress has been made in the preparation and application of stable Ge(II) compounds in coordination chemistry.<sup>2</sup> This has been achieved by judicious choice of sterically demanding substituents on the Ge(II) atom, which provide a kinetic and thermodynamic stabilization with  $\pi$ -donor groups bonded to the divalent germanium atom. Taking advantage of the intramolecular stabilization of coordination of nitrogen to low-valent germanium, a number of stable  $\beta$ -diketiminate germanium(II) complexes LGeX **A** (Scheme 1; L =  $\beta$ -diketiminate; X = halide, alkyl, hydride, hydroxide, alkoxide, and amide) have been synthesized,<sup>3,4</sup> among which LGeH,<sup>3g</sup> LGeCH<sub>3</sub>,<sup>3e</sup> and LGeOH<sup>3f</sup> deserve particular attention because of the small terminal groups and their remarkable electronic features. Recently, Power et al. described the first germanium(II) amide with the parent NH<sub>2</sub> group, which was obtained by reacting a corresponding terphenyl

Scheme 1



X = halide, hydride, alkyl, OR, NR<sub>2</sub>; Ar = 2,6-*i*Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>

nyl germanium(II) halide with liquid ammonia.<sup>5</sup> To our knowledge, a stable divalent germanium species featuring the parent phosphanide group PH<sub>2</sub> is unknown as yet, although a few bulky phosphanyl-substituted germylenes have been reported.<sup>6</sup>

Currently, we are particularly interested in structure–reactivity relationships of N-heterocyclic divalent group 14 element

\* Corresponding author. E-mail: matthias.driess@tu-berlin.de.

<sup>†</sup> Technische Universität Berlin.

<sup>‡</sup> Ruhr-Universität Bochum.

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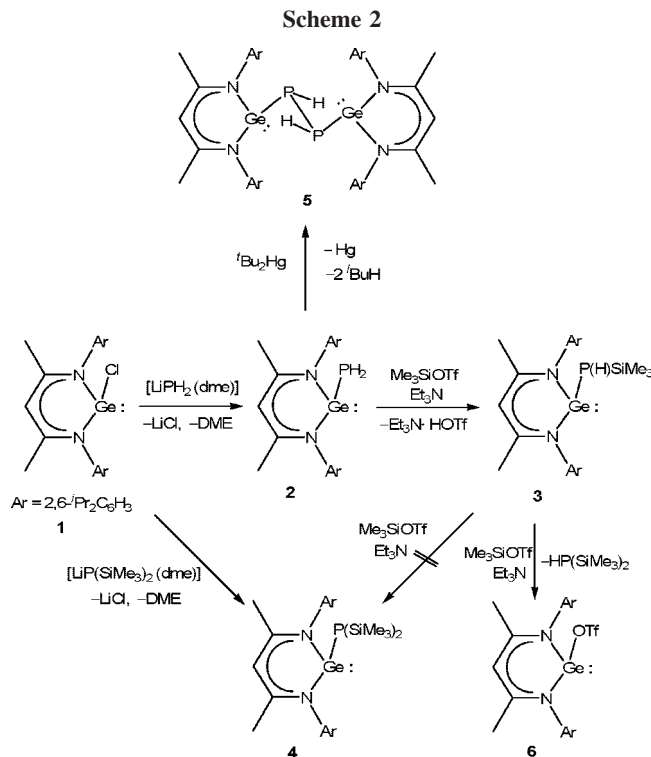
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complexes LEX (E = Si, Ge, Sn, and Pb; L = N-heterocyclic, monoanionic chelate ligands; X = alkoxide, amide, halide, phosphanide), which could serve as single-site initiators for the polymerization of lactides or/and Lewis acid catalysts for ring-opening polymerization.<sup>7</sup> Using the sterically encumbering  $\beta$ -diketiminato ligand, we have successfully synthesized a series of heteroleptic  $\beta$ -diketiminato complexes of lead(II) bearing terminal phenolato, bis(trimethylsilyl)amido, bis(trimethylsilyl)phosphanido, and silylidenephosphanido ligands.<sup>8</sup> Furthermore, we prepared the first silicon(II) analogues L(Si):R' (R' = siloxyl,<sup>9</sup> OTf,<sup>10</sup> B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>),<sup>11</sup> applying the zwitterionic silylene L'Si: (L' = CH[(C=CH<sub>2</sub>)CMe][N(aryl)]<sub>2</sub>; aryl = 2,6-*i*-Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>).<sup>10</sup> Interestingly, dark brown crystals of the Ge(II) homologue of the latter silylene, compound **B** (Scheme 1),<sup>12</sup> are also conveniently accessible through dehydrochlorination of LGeCl (**1**)<sup>3c</sup> with LiN(SiMe<sub>3</sub>)<sub>2</sub>. Furthermore, the betain-like germylene **B** reacts with 1,2-dibromoethane, affording the bis(bromogermylene) **C** (Scheme 1) as yellow crystals.<sup>12</sup> Here we report the synthesis and characterization of the first series of stable  $\beta$ -diketiminato germanium(II)-phosphanido complexes LGePH<sub>2</sub> (**2**), LGeP(H)SiMe<sub>3</sub> (**3**), LGeP(SiMe<sub>3</sub>)<sub>2</sub> (**4**), and LGeP(H)P(H)GeL (**5**) (L =  $\beta$ -diketiminato).

## Results and Discussion

**Synthesis.** The  $\beta$ -diketiminato-substituted chlorogermylene LGeCl (**1**)<sup>3c</sup> readily reacts with 1 molar equiv of [LiPH<sub>2</sub>(dme)] (dme = 1,2-dimethoxyethane) in diethyl ether at -50 °C to give a clear orange solution. The NMR spectroscopic data of the reaction mixture indicate that the desired phosphanyl-substituted germanium complex LGePH<sub>2</sub> (**2**) is formed nearly quantitatively after warming to room temperature and stirring overnight (Scheme 2). After extraction with *n*-hexane, compound **2** can be obtained in the form of orange crystals in 83% yield. Its composition and constitution are proven by elemental analysis and <sup>1</sup>H, <sup>13</sup>C, and <sup>31</sup>P NMR spectroscopy. In addition, the structure of **2** has been confirmed by single-crystal X-ray diffraction analysis (see below). While compound **2** is sensitive to oxygen and moisture, it is indefinitely stable under nitrogen atmosphere and survives prolonged heating of solutions even at 110 °C for several hours.

Compound **2** represents the first stable  $\beta$ -diketiminato germanium(II) complex with the parent phosphanide PH<sub>2</sub> group. Accordingly, it could serve as a convenient building block for other phosphane derivatives. This has been shown by simple silylation of the phosphorus atom. In fact, reaction of **2** with 1 molar equiv of trimethylsilyl triflate, Me<sub>3</sub>SiOTf, in the presence of triethylamine as auxiliary base in diethyl ether at -60 °C leads merely to LGeP(H)SiMe<sub>3</sub> (**3**) (Scheme 2). Compound **3**



has been isolated in the form of orange-brown cubes in 77% yield through extraction with *n*-hexane and recrystallization at -20 °C. Unexpectedly, attempts to prepare LGeP(SiMe<sub>3</sub>)<sub>2</sub> (**4**) by further silylation of the phosphorus in **3** with trimethylsilyl triflate failed. Instead, the reaction of **3** with 1 molar equiv of trimethylsilyl triflate leads merely to LGeOTf (**6**) and HP(SiMe<sub>3</sub>)<sub>2</sub>. Although the mechanism is still unknown, we believe that the latter products result from degradation of the corresponding phosphonium triflate ion pair [LGeP(H)(SiMe<sub>3</sub>)<sub>2</sub>]<sup>+</sup> OTf<sup>-</sup> as reactive intermediate. In line with that, the ease of Ge–P fission and replacement of HP(SiMe<sub>3</sub>)<sub>2</sub> by the relatively weak OTf<sup>-</sup> nucleophile reduces steric congestion and leads to the partially resonance stabilized LGe<sup>+</sup> cation<sup>4</sup> in the contact ion pair **6**.

Fortunately, compound **4** is accessible from salt metathesis reaction of **1** with the corresponding lithium phosphanide [LiP(SiMe<sub>3</sub>)<sub>2</sub>(dme)] (Scheme 2) and obtained in the form of pale yellow crystals in 89% yield. It is noteworthy that the reaction of **1** with the nitrogen analogue LiN(SiMe<sub>3</sub>)<sub>2</sub> leads solely to the zwitterionic germylene **B** by dehydrochlorination instead of a nucleophilic Cl/N(SiMe<sub>3</sub>)<sub>2</sub> substitution at germanium.<sup>12</sup> Apparently, the P(SiMe<sub>3</sub>)<sub>2</sub> anion is not strong enough to act as a corresponding base, and the voluntary Ge–P bond formation reflects the higher polarizability and nucleophilicity of phosphorus in contrast to nitrogen.

In order to prepare isolable heterobimetallic phosphanido complexes of Ge(II), we investigated the reactivity of **2** toward potential metalation reagents. However, attempts to metalate the terminal PH<sub>2</sub> group in **2** applying BuLi and Me<sub>2</sub>Zn, respectively, failed and led only to nucleophilic replacement of the PH<sub>2</sub> group and irrepressible side reactions. Interestingly, the preferential Ge–P fission in **2** through attack of organometallic reagents is hampered by using <sup>t</sup>Bu<sub>2</sub>Hg. However, the reaction of **2** with <sup>t</sup>Bu<sub>2</sub>Hg in hexane occurs only above 60 °C, affording the novel *P,P'*-bis(phosphanylgermylene) LGeP(H)P(H)GeL (**5**) and elemental Hg (Scheme 2). Compound **5** is obtained as brown-red crystals in 56% yield, which are sparingly soluble in hexane, but readily dissolve in toluene and ethereal solvents.

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Table 1. Comparison of Selected  $^1\text{H}$  and  $^{31}\text{P}$  NMR Data for 1–6

|                                                | 1 <sup>3c</sup> | 2               | 3                      | 4                                  | 5         | 6    |
|------------------------------------------------|-----------------|-----------------|------------------------|------------------------------------|-----------|------|
| Y                                              | Cl              | PH <sub>2</sub> | PH(SiMe <sub>3</sub> ) | P(SiMe <sub>3</sub> ) <sub>2</sub> | PH-PH-GeL | OTf  |
| $^1\text{H}$ NMR ( $\delta$ , ppm) $\gamma$ -H | 5.14            | 4.90            | 4.72                   | 5.04                               | 4.60      | 5.52 |
| $^1\text{H}$ NMR ( $\delta$ , ppm) P-H         |                 | 1.32            | -0.05                  |                                    | -1.48     |      |
| $^{31}\text{P}$ NMR ( $\delta$ , ppm)          |                 | -206.0          | -206.4                 | -192.7                             | -182.5    |      |
| $^1J_{\text{P,H}}$ (Hz)                        |                 | 172.7           | 172.0                  |                                    | 170.2     |      |

Although the mechanism is still unknown, it seems reasonable to assume that the formation of **5** proceeds via the elusive initial product  $\text{LGeP(H)Hg'Bu}$  and/or  $\text{LGeP(H)HgP(H)GeL}$  and isobutane. The latter reactive P–Hg intermediates readily decompose under reductive elimination of mercury and subsequent P–P bond formation to give **5**. Similar P–P bond formation under liberation of Hg has been observed by the reaction of primary and secondary phosphanes with  $^t\text{Bu}_2\text{Hg}$ <sup>13</sup> and decomposition of *P*-mercurio 1,3-diphospha-2,4-disiletanes to give 1,3-diphospha-2,4-disilabicyclo[1.1.0]butanes.<sup>14</sup>

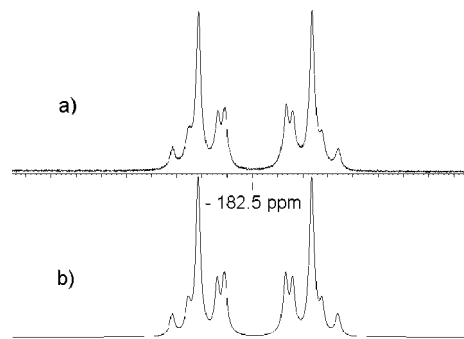
**NMR Spectroscopy.** In addition to EI-MS data and elemental analyses, the composition and constitution of **2**–**6** are supported by  $^1\text{H}$ ,  $^{13}\text{C}$ , and  $^{31}\text{P}$  NMR spectra. The  $^1\text{H}$  and  $^{13}\text{C}$  NMR resonance signals for the  $\beta$ -diketiminate ligand are similar to those observed for related Ge(II) complexes.<sup>3</sup> Notably, the ring-methine proton ( $\gamma$ -H) in **6** resonates at significantly lower field when compared with the corresponding resonances of the phosphanyl-substituted Ge(II) complexes **2**–**5** and that observed for **1**<sup>3</sup> (Table 1), indicating somewhat aromatic character of the  $\text{C}_3\text{N}_2\text{Ge}$   $\pi$ -ring system in **6** due to partial  $\text{LGe}^+\cdots\text{OTf}^-$  character.<sup>3h,12</sup>

The  $^1\text{H}$  and  $^{31}\text{P}$  NMR spectra of **2** confirm the presence of a  $\text{PH}_2$  group. Thus, the  $^1\text{H}$  NMR spectrum shows a doublet at 1.32 ppm with a  $^1J_{\text{P,H}}$  coupling constant of 172.7 Hz. In line with that, the  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum of **2** displays a singlet at -206.0 ppm, which degenerates into a triplet in the  $^{31}\text{P}$  spectrum with a similar  $^1J_{\text{P,H}}$  coupling constant of 172.7 Hz. The  $^{31}\text{P}$  nuclei in **2**–**5** are strongly shielded compared with the values observed for the monomeric diphosphanylgermylene [ $\{\text{Is}_2\text{FSi}\}(\text{Pr}_3\text{Si})\text{P}\}_2\text{Ge}$  ( $\text{Is} = 2,4,6\text{-}^i\text{Pr}_3\text{C}_6\text{H}_2$ ) (-62.1 ppm),<sup>6c</sup> the head-to-tail dimer  $\{(\text{Pr}_2\text{P})_2\text{Ge}\}_2$  (13.8, -36.8 ppm),<sup>6b</sup> and the intramolecularly base-stabilized diphosphanylgermylene [ $(\text{Me}_3\text{Si})_2\text{CH}\}(\text{C}_6\text{H}_4\text{-2-CH}_2\text{NMe}_2)\text{P}\}_2\text{Ge}$  (-45.8 ppm),<sup>6d</sup> indicating considerably polar character of the Ge–P  $\sigma$ -bond.

The monosilylated phosphane **3** displays a singlet at -206.4 ppm in the  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum and a doublet with a  $^1J_{\text{P,H}}$  coupling constant of 172.0 Hz in the  $^{31}\text{P}$  spectrum. The marginal change of the isotropic  $^{31}\text{P}$  chemical shift in comparison to **2** is somewhat unexpected, since silylation of phosphorus atoms leads usually to a higher shielding of the  $^{31}\text{P}$  nucleus due to

Si→P  $\sigma$ -donation.<sup>15,16</sup> In line with that, the phosphorus nucleus in the disilylphosphane **4** resonates at lower field (-192.7 ppm) in the  $^{31}\text{P}$  NMR spectrum in comparison with that of **3**, and the relatively small  $^1J_{\text{P,Si}}$  value of 17.1 Hz (vs 30.2 Hz for **3**) indicates a lower 3s contribution of phosphorus in the P–Si bond.<sup>15</sup> Remarkably, the P–H proton of the  $\text{PH}(\text{SiMe}_3)$  group in **3** displays a doublet in the  $^1\text{H}$  NMR spectrum at relatively high field (-0.05 ppm), with a drastic change of  $\Delta\delta = -1.37$  ppm in comparison with **2**. The  $^{31}\text{P}$  NMR spectrum of the *P,P'*-bis(phosphanylgermylene) **5** in toluene-*d*<sub>8</sub> shows a multiplet at -182.5 ppm, representing the X,X'-part of an AA'XX' system ( $\text{A,A}' = ^1\text{H}$ ;  $\text{X,X}' = ^{31}\text{P}$ ; Figure 1), whereas the  $^{31}\text{P}$  NMR spectrum gives a singlet at the same chemical shift. The corresponding proton resonance is centered at unusually high field at  $\delta -1.48$  in the  $^1\text{H}$  NMR spectrum, representing the A,A'-part of the AA'XX' splitting pattern and similar coupling constants. Unlike related alkyl- or aryl-substituted *P,P'*-diphosphanes obtained and compiled by Albrand and Taieb<sup>17</sup> showing resonances for both *rac* and *meso* diastereomers, only the *meso* isomer of **5** is observed in solution, which remains unchanged even in the temperature range from -60 to 60 °C. In order to determine the magnitudes of the coupling constants of the AA'XX' spin system ( $^1J_{\text{AX}}, ^2J_{\text{AX}'}, ^3J_{\text{AA}'}, ^1J_{\text{XX}'}$ ), a simulation of the spectrum was performed.<sup>18</sup> The experimental and calculated spectra are depicted in Figure 1a and b. While the  $^{31}\text{P}$  resonance shows a significantly downfield shift compared with those in **2**, **3**, and **4**, the  $^1J_{\text{P,H}}$  coupling constants differ only a little. Remarkably, the unusually small magnitude of the  $^1J_{\text{P,P}}$  coupling constant (64.7 Hz) is reminiscent of the situation in a strained  $\text{Si}_2\text{P}_4$  cage compound,<sup>19</sup> probably due to steric reasons.

**X-ray Structures.** Molecular structures of **2**–**6** were elucidated by single-crystal X-ray diffraction analysis. The ORTEP drawings of **2**–**6** are shown in Figures 2–6 together with their structural parameters. Corresponding data collection parameters



**Figure 1.** (a) Experimental  $^{31}\text{P}$  NMR spectrum of **5** in toluene-*d*<sub>8</sub> (298 K) at 161.97 MHz,  $\delta -182.5$ . (b) Simulated  $^{31}\text{P}$  NMR spectrum of **5** (X part of the AA'XX' spin pattern:  $^3J_{\text{H,H}} = 18.5$  Hz,  $^1J_{\text{P,H}} = 170.2$  Hz,  $^2J_{\text{P,H}} = 10.4$  Hz,  $^1J_{\text{P,P}} = 64.7$  Hz).

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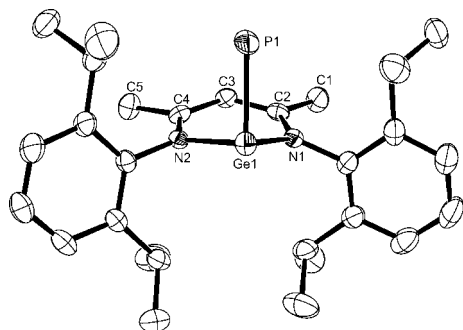
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**Figure 2.** Molecular structure of **2**. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [deg]: Ge1–N1 1.979(2), Ge1–N2 1.979(2), Ge1–P1 2.333(1), N1–C2 1.347(4), N2–C4 1.335(4), C2–C3 1.391(4), C3–C4 1.398(4), N1–Ge1–N2 91.4(1), N1–Ge1–P1 93.45(7), N2–Ge1–P1 92.86(7), C2–N1–Ge1 122.9(2), C4–N2–Ge1 123.3(2), N1–C2–C3 122.5(3), C2–C3–C4 127.5(3), N2–C4–C3 122.9(3).

and refinement statistics are listed in Table 3, and selected interatomic distances and angles are given in Table 2. While compound **2** crystallizes in the monoclinic space group  $P2_1/c$ , the compounds **3**, **4**, and **6** crystallize in the monoclinic space group  $P2_1/n$ . Compound **5** crystallizes in the triclinic space group  $P\bar{1}$  with a crystallographic center of inversion midway between the two phosphorus atoms, representing the *meso* configuration, similar to the configuration of **5** obtained in solution.

The compounds **2–6** consist of differently puckered six-membered  $C_3N_2Ge$  rings with folding angles ranging from 22.1° to 40.8° (Table 2). The Ge centers are three-coordinated and adopt a pyramidal geometry. The sums of bond angles around the Ge center range from 274.5° to 288.6°, and the degree of pyramidalization (DP) ranges from 79% to 95% (Table 2),<sup>20</sup> illustrating the high 4p-character of the germanium  $\sigma$ -orbitals in the Ge–X (X = O, P) bonds. In other words, the vertex of the germanium atom is occupied by a lone pair of electrons with pronounced 4s-character.

The structure feature of compound **2** is reminiscent of the starting material  $LGeCl$ , **1**.<sup>3c</sup> The Ge–N bond length of 1.979(2) Å in **2** is very close to those observed in **1** [1.988(2), 1.997(3) Å]. The Ge–P bond length of 2.333(1) Å in **2** lies between the corresponding values seen in  $(C_6F_5)_3GePH_2$  (2.307 Å)<sup>16</sup> and in the four-membered  $Ge_2P_2$  ring [ $[Bu(mes)GePH]_2$  (2.348 Å), having four-coordinate germanium atoms. As expected, the Ge(IV)–P distances are significantly shorter than those values reported for Ge(II)–P compounds. For example, the Ge(II)–P distances in the dimeric  $\{(Pr_2P)_2Ge\}_2$  are 2.426(1), 2.422(1), and 2.398(1) Å,<sup>6b</sup> respectively, and the corresponding values in the intramolecularly base-stabilized diphosphanylgermylene  $\{[(Me_3Si)_2CH](C_6H_4-2-CH_2NMe_2)P\}_2Ge$  amount to 2.4023(4) and 2.4114(4) Å, respectively.<sup>6d</sup>

The monosilylated derivative **3** has a structural feature significantly different from that of the parent phosphanyl compound **2**. The folding angle between the planes defined by the N1, C2, C3, C4, N2 atoms (plane 1) and the N1, Ge1, N2 atoms (plane 2) of 40.8° is much greater than that observed for **2** (26.0°). Furthermore, the  $P(H)SiMe_3$  moiety is bent away from plane 1 in **3**, in contrast to the orientation of the  $PH_2$  group in **2**. Interestingly, compound **4** (folding angle 22.1°) shows a

structural feature similar to that of **2**, whereas compound **5** (folding angle 40.6°) again adopts a strongly puckered  $C_3N_2Ge$  cycle, as observed for **3**. The different structural features of **3** and **5** are presumably due to the pyramidal nature of secondary phosphanes and steric congestion around phosphorus. Going to an almost planar configuration at phosphorus may change the orientation of the phosphanyl group again. In fact, the phosphorus atom in the  $P(SiMe_3)_2$  group has a very low inversion barrier,<sup>15,16,22</sup> leading to an almost planar trigonal coordination mode of phosphorus with the respective sum of angles of 355.2° in **4**. Thus, the almost planar  $P(SiMe_3)_2$  moiety in **4** favors a similar orientation of the phosphanyl group toward the puckered  $C_3N_2Ge$  ring to that in **2**. The Ge–P distances in **3** [2.4261(7) Å], **4** [2.3912(8) Å], and **5** [2.408(2) Å] lie in the range of previously reported Ge(II)–P distances of  $\{(Pr_2P)_2Ge\}_2$  and  $\{[(Me_3Si)_2CH](C_6H_4-2-CH_2NMe_2)P\}_2Ge$ , ranging from 2.398(1) to 2.426(1) Å.<sup>6b,d</sup> However, the latter are longer than the corresponding value observed in **2** [2.333(1) Å] owing to steric congestion. In line with that, the Ge–N bond lengths in **3** [2.017(2) Å], **4** [2.006(2), 2.046(2) Å], and **5** [2.028(5), 2.033(5) Å] are also slightly longer than that in **2** [1.979(2) Å].

In spite of the sterically encumbered  $LGe$  moieties in the  $P,P'$ -bis(phosphanylgermylene) **5**, the P–P distance of 2.221(4) Å is very close to that in  $P_4$  (2.20 Å). The latter is also similar to the corresponding values in  $(mes)PH-PH(mes)$  (2.229 Å),<sup>23</sup>  $\{(2-C_5H_3N-6-Me)(Me_3Si)_2C\}P(H)-P(H)\{C(SiMe_3)_2(2-C_5H_3N-6-Me)\}$  (2.222 Å),<sup>24</sup> and  $(Me_3Si)_2C(H)PH-PHC(H)(SiMe_3)_2$  (2.209 Å),<sup>25</sup> respectively, which represent rare examples of PH-terminated diphosphanes not yet structurally characterized.

The structure of the triflate complex **6** is practically identical with that of a related diketiminate Ge(II) triflate,<sup>12</sup> which results from 1,4-addition reaction of  $Me_3SiOTf$  to the germylene **B** (Scheme 1). The rather long Ge–O(triflate) distance indicates a pronounced tendency to a  $(LGe)^+ \cdots OTf^-$  ion pair separation: the Ge1–O1 distance of 2.151(3) Å is slightly longer than the value in the similar 1,4-addition product of  $Me_3SiOTf$  to **B** [2.082(1) Å].<sup>12</sup> The latter distances are much longer than typical covalent Ge–O bonds in germoxanes (175–185 Å),<sup>26</sup> but shorter than the sum of the van der Waals radii of Ge(II) and oxygen (3.67 Å).<sup>27</sup> In line with the cationic character of  $LGe^+$ , the Ge–N bond lengths in **6** [1.931(4) and 1.932(4) Å] are significantly shorter than the corresponding values in **1** [1.988(2) Å]<sup>3c</sup> and only slightly longer than those observed in the noncoordinated  $LGe^+$  cation [1.894(2) Å] in a related borate salt.<sup>4</sup>

## Conclusion

The first heteroleptic  $\beta$ -diketiminato complex of germanium(II) with a terminal  $PH_2$  group, compound **2**, was successfully synthesized and characterized structurally. The latter

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Table 2. Selected Metrical Parameters for 2–6 (distances in Å and angles in deg)

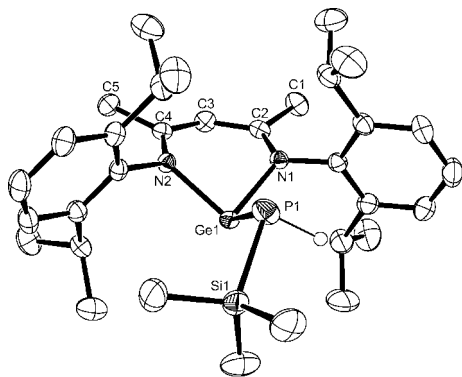
|                                                   | 2        | 3         | 4         | 5        | 6        |
|---------------------------------------------------|----------|-----------|-----------|----------|----------|
| Ge1–P1                                            | 2.333(1) | 2.4261(7) | 2.3912(8) | 2.408(2) |          |
| Ge1–N1                                            | 1.979(2) | 2.017(2)  | 2.046(2)  | 2.033(5) | 1.931(4) |
| Ge1–N2                                            | 1.979(2) | 2.017(2)  | 2.006(2)  | 2.028(5) | 1.932(4) |
| N1–C2                                             | 1.347(4) | 1.325(3)  | 1.344(4)  | 1.313(7) | 1.348(5) |
| N2–C4                                             | 1.335(4) | 1.330(2)  | 1.313(4)  | 1.301(7) | 1.343(6) |
| C3–C2                                             | 1.391(4) | 1.405(3)  | 1.393(4)  | 1.407(9) | 1.385(6) |
| C3–C4                                             | 1.398(4) | 1.401(3)  | 1.405(4)  | 1.412(9) | 1.383(7) |
| N1–Ge1–N2                                         | 91.4(1)  | 88.58(7)  | 90.20(9)  | 87.9(2)  | 93.0(2)  |
| sum of angles at Ge                               | 277.7    | 283.8     | 288.6     | 285.0    | 274.5    |
| sum of angles at P                                |          | 280.0     | 355.2     | 277.1    |          |
| degree of pyramidalization at Ge (%) <sup>a</sup> | 91       | 85        | 79        | 83       | 95       |
| folding angle <sup>b</sup>                        | 26.0     | 40.8      | 22.1      | 40.6     | 24.4     |

<sup>a</sup> Reference 20. <sup>b</sup> Between the planes defined by the N1, C2, C3, C4, N2 atoms (plane 1) and the N1, Ge1, N2 atoms (plane 2).

Table 3. Crystal Data Collection and Refinement Details for the Crystal Structures

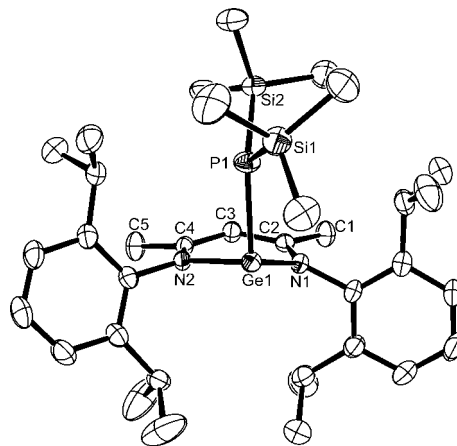
|                                                           | 2                                                  | 3                                                    | 4·2C <sub>5</sub> H <sub>10</sub>                                 | 5                                                                             | 6                                                                                |
|-----------------------------------------------------------|----------------------------------------------------|------------------------------------------------------|-------------------------------------------------------------------|-------------------------------------------------------------------------------|----------------------------------------------------------------------------------|
| formula                                                   | C <sub>29</sub> H <sub>41</sub> GeN <sub>2</sub> P | C <sub>32</sub> H <sub>51</sub> GeN <sub>2</sub> PSi | C <sub>45</sub> H <sub>79</sub> GeN <sub>2</sub> PSi <sub>2</sub> | C <sub>58</sub> H <sub>84</sub> Ge <sub>2</sub> N <sub>4</sub> P <sub>2</sub> | C <sub>30</sub> H <sub>41</sub> F <sub>3</sub> GeN <sub>2</sub> O <sub>3</sub> S |
| molecular weight                                          | 521.20                                             | 595.40                                               | 807.84                                                            | 1044.41                                                                       | 639.30                                                                           |
| cryst size, mm <sup>3</sup>                               | 0.6 × 0.5 × 0.4                                    | 0.6 × 0.6 × 0.6                                      | 0.6 × 0.4 × 0.4                                                   | 0.4 × 0.3 × 0.3                                                               | 0.4 × 0.4 × 0.4                                                                  |
| cryst syst                                                | monoclinic                                         | monoclinic                                           | monoclinic                                                        | triclinic                                                                     | monoclinic                                                                       |
| space group                                               | P2 <sub>1</sub> /c                                 | P2 <sub>1</sub> /n                                   | P2 <sub>1</sub> /n                                                | P1                                                                            | P2 <sub>1</sub> /n                                                               |
| a, Å                                                      | 14.1380(5)                                         | 8.9098(4)                                            | 11.5933(4)                                                        | 10.8175(6)                                                                    | 12.087(2)                                                                        |
| b, Å                                                      | 16.3244(6)                                         | 19.6084(9)                                           | 22.8578(9)                                                        | 12.0783(7)                                                                    | 13.013(3)                                                                        |
| c, Å                                                      | 13.8086(5)                                         | 19.6505(10)                                          | 18.3221(7)                                                        | 12.6434(7)                                                                    | 24.046(5)                                                                        |
| α, deg                                                    | 90.00                                              | 90.00                                                | 90.00                                                             | 91.550(2)                                                                     | 90.00                                                                            |
| β, deg                                                    | 116.3790(10)                                       | 90.3640(10)                                          | 93.2330(10)                                                       | 108.361(2)                                                                    | 92.11(3)                                                                         |
| γ, deg                                                    | 90.00                                              | 90.00                                                | 90.00                                                             | 111.339(2)                                                                    | 90.00                                                                            |
| V, Å <sup>3</sup>                                         | 2855.10(18)                                        | 3433.0(3)                                            | 4847.6(3)                                                         | 1441.49(14)                                                                   | 3779.6(13)                                                                       |
| Z                                                         | 4                                                  | 4                                                    | 4                                                                 | 1                                                                             | 4                                                                                |
| ρ, Mg/m <sup>3</sup>                                      | 1.213                                              | 1.152                                                | 1.107                                                             | 1.203                                                                         | 1.123                                                                            |
| μ, mm <sup>−1</sup>                                       | 1.147                                              | 0.995                                                | 0.744                                                             | 1.136                                                                         | 0.907                                                                            |
| temperature, K                                            | 173(2)                                             | 173(2)                                               | 173(2)                                                            | 173(2)                                                                        | 173(2)                                                                           |
| θ limit, deg                                              | 1.61–25.00                                         | 1.47–30.63                                           | 1.43–25.00                                                        | 1.72–24.99                                                                    | 1.69–25.00                                                                       |
| no. of measd reflns                                       | 17 566                                             | 32 207                                               | 29 934                                                            | 9145                                                                          | 22 709                                                                           |
| no. of indep reflns                                       | 5029 [R(int) = 0.0895]                             | 10 538 [R(int) = 0.0768]                             | 8532 [R(int) = 0.0647]                                            | 5063 [R(int) = 0.1193]                                                        | 6653 [R(int) = 0.0889]                                                           |
| goodness of fit                                           | 1.050                                              | 1.042                                                | 1.133                                                             | 0.963                                                                         | 0.930                                                                            |
| no. of data, restraints, params                           | 5029, 0, 308                                       | 10 538, 0, 351                                       | 8532, 10, 476                                                     | 5063, 0, 312                                                                  | 6653, 76, 393                                                                    |
| final R1, wR2 <sup>a</sup>                                | 0.0449, 0.1300                                     | 0.0519, 0.1321                                       | 0.0463, 0.1259                                                    | 0.0721, 0.1739                                                                | 0.0591, 0.1561                                                                   |
| Δρ <sub>max</sub> , Δρ <sub>min</sub> , e Å <sup>−3</sup> | 1.201, −0.820                                      | 0.845, −0.676                                        | 0.640, −0.562                                                     | 1.190, −1.023                                                                 | 0.549, −0.498                                                                    |

<sup>a</sup> The value of R1 is based on selected data with  $F > 4\sigma(F)$ ; the value of wR2 is based on all data.



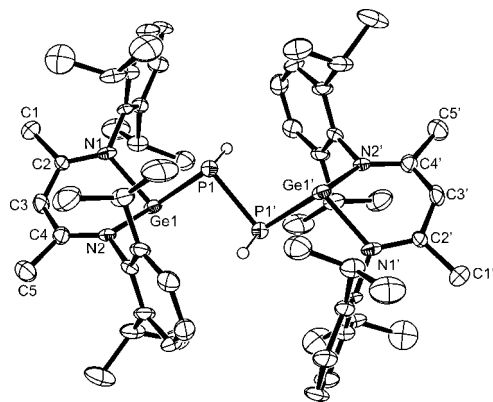
**Figure 3.** Molecular structure of **3**. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms, except that at P1, are omitted for the sake of clarity. Selected bond lengths [Å] and angles [deg]: Ge1–N1 2.017(2), Ge1–N2 2.017(2), Ge1–P1 2.426(7), P1–Si1 2.2366(9), N1–C2 1.325(3), N2–C4 1.330(2), C2–C3 1.405(3), C3–C4 1.401(3), N1–Ge1–N2 88.58(7), N1–Ge1–P1 94.57(5), N2–Ge1–P1 100.55(5), Si1–P1–Ge1 100.98(3), C2–N1–Ge1 118.7(1), C4–N2–Ge1 118.5(1), N1–C2–C3 122.5(2), C4–C3–C2 126.5(2), N2–C4–C3 122.8(2).

complex is unexpectedly stable and suitable for silylation at phosphorus to give the monosilylated derivative **3**. Further silylation of **3** leads to the cleavage of the Ge–P bond and formation of the Ge(II) triflate **6**. However, the doubly P-silylated compound **4** is simply accessible by salt metathesis reaction of LGeCl (**1**) with LiP(SiMe<sub>3</sub>)<sub>2</sub>. Reductive P–P

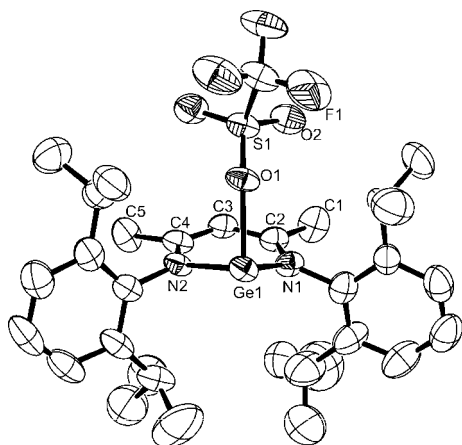


**Figure 4.** Molecular structure of **4**. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [deg]: Ge1–N1 2.006(2), Ge1–N2 2.046(2), Ge1–P1 2.3912(8), P1–Si1 2.219(1), P1–Si2 2.227(1), N1–C2 1.344(4), N2–C4 1.313(4), C2–C3 1.393(4), C3–C4 1.405(4), N1–Ge1–N2 90.20(9), N1–Ge1–P1 103.46(7), N2–Ge1–P1 94.93(6), Si1–P1–Si2 110.13(5), Si1–P1–Ge1 111.14(4), Si2–P1–Ge1 133.93(4), C2–N1–Ge1 124.2(2), C4–N2–Ge1 124.0(2), N1–C2–C3 122.3(2), N1–C2–C1 119.7(2), C2–C3–C4 127.7(3), N2–C4–C3 123.8(2).

coupling and dehydrogenation of **2** have been achieved by the reaction of 'Bu<sub>2</sub>Hg with **2**, leading to the novel *P,P'*-bis(phosphanylgermylene) **5**. The sterically encumbered novel ger-



**Figure 5.** Molecular structure of **5**. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms, except those at P1 and P1', are omitted for clarity. Symmetry transformation used to generate the equivalent atoms labeled with ('):  $1-x, -y+1, -z$ . Selected distances [Å] and angles [deg]: Ge1–N2 2.028(5), Ge1–N1 2.033(5), Ge1–P1 2.408(2), P1–P1' 2.221(4), N1–C2 1.313(7), N2–C4 1.301(7), C2–C3 1.407(9), C3–C4 1.412(9), N2–Ge1–N1 87.9(2), N2–Ge1–P1 98.4(2), N1–Ge1–P1 98.7(2), P1'–P1–Ge1 93.1(1), C2–N1–Ge1 118.8(4), C4–N2–Ge1 119.4(4), N1–C2–C3 122.1(6), C2–C3–C4 127.1(6), N2–C4–C3 122.3(6).



**Figure 6.** Molecular structure of **6**. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [deg]: Ge1–N1 1.931(4), Ge1–N2 1.932(4), Ge1–O1 2.151(3), N1–C2 1.348(5), N2–C4 1.343(6), C2–C3 1.385(6), C3–C4 1.383(7), N1–Ge1–N2 93.0(2), N1–Ge1–O1 91.8(1), N2–Ge1–O1 89.7(1), C2–N1–Ge1 122.8(3), C4–N2–Ge1 123.3(3), N1–C2–C3 122.5(5), C4–C3–C2 127.3(4), N2–C4–C3 122.9(4).

mylene-phosphane complexes **2–5** represent a fascinating new type of strong  $\sigma$ -donor phosphane ligands capable of synthesizing low-coordinate transition-metal complexes with potential application in homogeneous catalysis. Respective investigations are currently underway.

## Experimental Section

**General Considerations.** All experiments and manipulations were carried out under dry oxygen-free nitrogen using standard Schlenk techniques or in an MBraun inert atmosphere drybox containing an atmosphere of purified nitrogen. Solvents were dried by standard methods and freshly distilled prior to use. The starting

material LGeCl, **1**,<sup>3c</sup> [LiPH<sub>2</sub>(dme)],<sup>28</sup> [LiP(SiMe<sub>3</sub>)<sub>2</sub>(dme)],<sup>29</sup> and 'Bu<sub>2</sub>Hg<sup>30</sup> were prepared according to literature procedures. Me<sub>3</sub>SiOTf was purchased from Aldrich and used as received. The NMR spectra were recorded on Bruker spectrometers AS 200 and AV 400 with residual solvent signals as internal reference (<sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H}) or with an external reference (SiMe<sub>4</sub> for <sup>29</sup>Si, BF<sub>3</sub>·Et<sub>2</sub>O for <sup>19</sup>F, and 85% H<sub>3</sub>PO<sub>4</sub> for <sup>31</sup>P, respectively). Abbreviations: s = singlet; d = doublet; t = triplet; sept = septet; mult = multiplet; br = broad.

**LGePH<sub>2</sub> (2).** A solution of LGeCl (**1**) (1.89 g, 3.60 mmol) in diethyl ether (30 mL) was added to a suspension of [LiPH<sub>2</sub>(dme)] (0.47 g, 3.60 mmol) in diethyl ether (40 mL) with stirring at  $-50$  °C. The color of the solution turned immediately from yellow to orange. After 4 h stirring, the reaction mixture was allowed to slowly warm to room temperature and stirred overnight. Volatiles were removed *in vacuo*, and the residue was extracted with *n*-hexane (100 mL). Filtration and subsequent concentration (to about 30 mL) led, after 2 days of slow cooling to  $-20$  °C, to the isolation of orange crystals of **2** (1.14 g). After concentration of the supernatant to about 10 mL and cooling to  $-20$  °C for a further 2 days, an additional crop of **2** was isolated, affording a total yield of 1.57 g (83%). Mp:  $130$ – $134$  °C (dec). <sup>1</sup>H NMR (200.13 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K):  $\delta$  1.13 (d, <sup>3</sup>J<sub>HH</sub> = 6.8 Hz, 6 H, CH MeMe), 1.19 (d, <sup>3</sup>J<sub>HH</sub> = 6.8 Hz, 6 H, CH MeMe), 1.30 (d, <sup>3</sup>J<sub>HH</sub> = 6.8 Hz, 6 H, CH MeMe), 1.32 (d, <sup>1</sup>J<sub>PH</sub> = 173 Hz, 2 H, P H<sub>2</sub>), 1.47 (d, <sup>3</sup>J<sub>HH</sub> = 6.8 Hz, 6 H, CH MeMe), 1.54 (s, 6 H, NC Me), 3.47 (sept, <sup>3</sup>J<sub>HH</sub> = 6.8 Hz, 2 H, C HMe<sub>2</sub>), 3.66 (sept, d, <sup>3</sup>J<sub>HH</sub> = 6.8 Hz, <sup>1</sup>J<sub>PH</sub> = 2 Hz, 2 H, C HMe<sub>2</sub>), 4.90 (s, 1 H,  $\gamma$ -C H), 7.04–7.18 (m, br, 6 H, 2,6-<sup>i</sup>Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (50.32 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K):  $\delta$  23.3, 24.7, 24.8, 26.0, 26.1, 26.2, 28.7, 28.9, 29.1 (NC Me, CH Me); 98.8 ( $\gamma$ -C); 124.7, 124.8, 127.4, 140.5, 145.0, 145.2 (N C, 2,6-<sup>i</sup>Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>). <sup>31</sup>P{<sup>1</sup>H} NMR (161.97 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K):  $\delta$   $-206.0$  (s). <sup>31</sup>P NMR (161.97 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K):  $\delta$   $-206.0$  (t, <sup>1</sup>J<sub>PH</sub> = 172.7 Hz). IR (KBr, cm<sup>-1</sup>): 755 (m), 764 (m), 850 (m), 934 (m), 1021 (m), 1038 (m), 1058 (w), 1099 (m), 1110 (m), 1168 (m), 1258 (s), 1314 (s), 1359 (s), 1365 (s), 1385 (s), 1435 (s), 1459 (s), 1466 (s), 1520 (s), 1556 (s), 2299 (m, *P*–H *str.*), 2866 (s), 2924 (s), 2965 (s), 3058 (m). Anal. Calcd for C<sub>29</sub>H<sub>43</sub>N<sub>2</sub>GeP: C, 66.6; H, 8.3; N, 5.3. Found: C, 66.4; H, 8.7; N, 5.1. EI-MS: *m/z* (%): 490.3(25, [M – PH<sub>2</sub>]<sup>+</sup>), 475.2(8, [M – PH<sub>2</sub> – Me]<sup>+</sup>).

**LGeP(H)PSiMe<sub>3</sub> (3).** To a precooled ( $-60$  °C) Schlenk flask containing a solution of **2** (1.28 g, 2.45 mmol) in diethyl ether (12 mL) and triethylamine (0.70 mL, 4.90 mmol) was dropwise added trimethylsilyl triflate (0.55 g, 2.45 mmol) with stirring. The color of the solution turned gradually from orange to brown-red. After 2 h stirring, the reaction mixture was allowed to slowly warm to room temperature and stirred overnight. Volatiles were removed *in vacuo*, and the residue was extracted with *n*-hexane (15 mL). Concentration and storage of the brown-red extract in a  $-20$  °C freezer for 2 days afforded brown-red crystals of **3**. Yield: 1.12 g (77%). Mp:  $136$ – $140$  °C. <sup>1</sup>H NMR (400.13 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K):  $\delta$   $-0.05$  (d, <sup>1</sup>J<sub>PH</sub> = 171 Hz, 1 H, PHSiMe<sub>3</sub>),  $-0.02$  (d, <sup>3</sup>J<sub>PH</sub> = 3.2 Hz, 9 H, SiMe<sub>3</sub>), 1.12 (d, <sup>3</sup>J<sub>HH</sub> = 6.8 Hz, 6 H, CHMeMe), 1.19 (d, <sup>3</sup>J<sub>HH</sub> = 6.8 Hz, 6 H, CHMeMe), 1.36 (d, <sup>3</sup>J<sub>HH</sub> = 6.8 Hz, 6 H, CHMeMe), 1.51 (s, 6 H, NCMe), 1.65 (d, <sup>3</sup>J<sub>HH</sub> = 6.8 Hz, 6 H, CHMeMe), 3.37 (sept, <sup>3</sup>J<sub>HH</sub> = 6.8 Hz, 2 H, CHMe<sub>2</sub>), 3.94 (sept, <sup>3</sup>J<sub>HH</sub> = 6.8 Hz, 2 H, CHMe<sub>2</sub>), 4.72 (s, 1 H,  $\gamma$ -CH), 7.03–7.17 (m, br, 6 H, 2,6-<sup>i</sup>Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (100.61 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K):  $\delta$  2.9 (d, <sup>2</sup>J<sub>PC</sub> = 8.8 Hz, PHSiMe<sub>3</sub>); 23.0, 24.6, 24.8, 24.8, 24.9, 25.2, 26.8, 28.9, 29.0, 29.1 (NCMe, CHMe); 96.6 ( $\gamma$ -C); 124.6, 124.8, 127.2, 140.2, 144.3, 145.7 (2,6-<sup>i</sup>Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>); 167.2 (NC). <sup>31</sup>P{<sup>1</sup>H} NMR (161.97 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K):  $\delta$   $-206.4$  (s). <sup>31</sup>P NMR (161.97 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K):  $\delta$   $-206.4$  (d, <sup>1</sup>J<sub>PH</sub> = 172 Hz).

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$^{29}\text{Si}\{^1\text{H}\}$  NMR (79.49 MHz,  $\text{C}_6\text{D}_6$ , 298 K):  $\delta$  3.7 (d,  $^1J_{\text{PSi}} = 30.2$  Hz). IR (KBr,  $\text{cm}^{-1}$ ): 444 (m), 626 (m), 748 (m), 758 (m), 794 (s), 804 (m), 834 (s), 843 (s), 928 (m), 933 (m), 1015 (m), 1059 (m), 1098 (m), 1108 (m), 1176 (m), 1228 (w), 1243 (m), 1254 (m), 1320 (s), 1355 (s), 1374 (s), 1383 (s), 1437 (s), 1462 (s), 1488 (m), 1518 (s), 1560 (s), 2244 (m, *P-H str.*), 2867 (s), 2889 (m), 2925 (s), 2960 (s), 3060 (w). Anal. Calcd for  $\text{C}_{32}\text{H}_{51}\text{N}_2\text{GePSi}$ : C, 64.5; H, 8.6; N, 4.7. Found: C, 64.0; H, 8.7; N, 4.4. EI-MS:  $m/z$  (%) 595.4 (0.9,  $\text{M}^+$ ), 580.3 (2.5,  $[\text{M} - \text{Me}]^+$ ), 490.2 (100,  $[\text{M} - \text{PHSiMe}_3]^+$ ).

**LGeP(SiMe<sub>3</sub>)<sub>2</sub> (4).** A solution of **1** (1.60 g, 3.04 mmol) in diethyl ether (30 mL) was added to a solution of  $[\text{LiP}(\text{SiMe}_3)_2(\text{dme})]$  (0.84 g, 3.04 mmol) in diethyl ether (30 mL) with stirring at  $-20^\circ\text{C}$ . After 4 h stirring, the reaction mixture was allowed to slowly warm to room temperature and stirred overnight. Volatiles were removed *in vacuo*, and the residue was extracted with *n*-hexane (60 mL). Filtration and subsequent concentration (to about 8 mL) led, after 2 days of slow cooling to  $5^\circ\text{C}$ , to the isolation of pale yellow crystals of **4** (1.79 g, 89%). Mp:  $125^\circ\text{C}$  (dec).  $^1\text{H}$  NMR (200.13 MHz,  $\text{C}_6\text{D}_6$ , 298 K):  $\delta$  0.43 (d,  $^3J_{\text{PH}} = 4.6$  Hz, 18 H, Si Me<sub>3</sub>), 1.07 (d,  $^3J_{\text{HH}} = 6.8$  Hz, 6 H, CHMeMe), 1.27 (d,  $^3J_{\text{HH}} = 6.8$  Hz, 6 H, CHMeMe), 1.29 (d,  $^3J_{\text{HH}} = 6.8$  Hz, 6 H, CHMeMe), 1.52 (d,  $^3J_{\text{HH}} = 6.8$  Hz, 6 H, CHMeMe), 1.58 (s, 6 H, NCMe), 3.39 (sept,  $^3J_{\text{HH}} = 6.8$  Hz, 2 H, CHMe<sub>2</sub>), 3.89 (sept, of d,  $^3J_{\text{HH}} = 6.8$  Hz,  $J_{\text{PH}} = 1.7$  Hz, 2 H, CHMe<sub>2</sub>), 5.04 (s, 1 H,  $\gamma\text{-CH}$ ), 7.05–7.24 (m, br, 6 H, 2,6- $^i\text{Pr}_2\text{C}_6\text{H}_3$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR (50.32 MHz,  $\text{C}_6\text{D}_6$ , 298 K):  $\delta$  5.5 (d,  $^2J_{\text{PC}} = 10.4$  Hz,  $\text{P}[\text{SiMe}_3]_2$ ), 24.1 (NCMe), 24.7, 24.9, 25.2, 29.3 (CHMe<sub>2</sub>), 28.2 (d,  $J_{\text{PC}} = 5.0$  Hz), 29.4 (CHMe), 101.4 ( $\gamma\text{-C}$ ), 124.4, 125.5, 141.2, 144.3, 147.2 (2,6- $^i\text{Pr}_2\text{C}_6\text{H}_3$ ), 166.3 (NC).  $^{31}\text{P}\{^1\text{H}\}$  NMR (161.97 MHz,  $\text{C}_6\text{D}_6$ , 298 K):  $\delta$  -192.7 (s).  $^{29}\text{Si}\{^1\text{H}\}$  NMR (79.49 MHz,  $\text{C}_6\text{D}_6$ , 298 K):  $\delta$  2.0 (d,  $^1J_{\text{PSi}} = 17.1$  Hz). IR (KBr,  $\text{cm}^{-1}$ ): 439 (m), 483 (m), 628 (s), 680 (w), 744 (m), 757 (m), 794 (s), 833 (s), 846 (s), 937 (w), 1021 (w), 1108 (w), 1168 (m), 1239 (s), 1259 (m), 1286 (w), 1316 (s), 1360 (s), 1384 (s), 1461 (s), 1525 (s), 2869 (m), 2891 (m), 2928 (s), 2963 (s), 3061 (w). Anal. Calcd for  $\text{C}_{35}\text{H}_{59}\text{N}_2\text{GePSi}_2$ : C, 63.0; H, 8.9; N, 4.2. Found: C, 62.9; H, 8.4; N, 4.0. EI-MS:  $m/z$  (%) 667.6 (8,  $\text{M}^+$ ), 579.4 (5,  $[\text{M} - \text{SiMe}_3 - \text{Me}]^+$ ), 490.3 (22,  $[\text{M} - \text{P}(\text{SiMe}_3)_2]^+$ ).

**LGeP(H)P(H)GeL (5).** An aluminum foil-wrapped Schlenk flask was charged with  $\text{LGePH}_2$  (0.43 g, 0.82 mmol) and  $^t\text{Bu}_2\text{Hg}$  (0.26 g, 0.82 mmol) in hexane (20 mL). This mixture was allowed to warm to  $60^\circ\text{C}$  with stirring for 48 h, and a gray precipitate of elementary Hg was formed. After decantation, the brown-red solution was slowly cooled to room temperature to afford brown-red crystals of **5**. Yield: 0.24 g (56%). Mp:  $210^\circ\text{C}$  (dec).  $^1\text{H}$  NMR (400.13 MHz, toluene- $d_8$ , 298 K):  $\delta$  -1.48 (A part of the AA'XX' spin pattern:  $^3J_{\text{H,H}} = 18.5$  Hz,  $^1J_{\text{P,H}} = 170.2$  Hz,  $^2J_{\text{P,H}} = 10.4$  Hz,  $^1J_{\text{P,P}} = 64.7$  Hz), 1.10–1.65 (br  $\text{NCCH}_3$ , CHMeMe), 3.27 (br 2H, CHMe<sub>2</sub>), 3.65 (br 2H, CHMe<sub>2</sub>), 4.60 (s, 1 H,  $\gamma\text{-CH}$ ), 6.65–7.66 (m, br, 6 H, 2,6- $^i\text{Pr}_2\text{C}_6\text{H}_3$ ).  $^{31}\text{P}\{^1\text{H}\}$  NMR (161.97 MHz, toluene- $d_8$ , 298 K):  $\delta$  -182.5 (s).  $^{31}\text{P}$  NMR (161.97 MHz, toluene- $d_8$ ,

298 K):  $\delta$  -182.5 (see Figure 1). IR (KBr,  $\text{cm}^{-1}$ ): 442 (w), 758 (m), 796 (m), 858 (w), 902 (w), 1020 (m), 1058 (w), 1101 (w), 1144 (w), 1172 (w), 1228 (w), 1258 (m), 1318 (s), 1376 (s), 1384 (s), 1438 (s), 1464 (m), 1529 (s), 2867 (m), 2926 (m), 2962 (s), 3059 (w). Anal. Calcd for  $\text{C}_{58}\text{H}_{84}\text{N}_4\text{Ge}_2\text{P}_2$ : C, 66.7; H, 8.1; N, 5.4. Found: C, 66.9; H, 7.9; N, 5.2. EI-MS:  $m/z$  (%) 1044.5 (0.04,  $\text{M}^+$ ), 490.25 (38,  $[\text{1/2M} - \text{PH}]^+$ ), 475.3 (24,  $[\text{1/2M} - \text{PH} - \text{Me}]^+$ ).

**LGeOTf (6).** To a precooled ( $-60^\circ\text{C}$ ) Schlenk flask containing a solution of  $\text{LGePH}_2$  (0.44 g, 0.84 mmol) in diethyl ether (10 mL) and triethylamine (0.46 mL, 3.36 mmol) was dropwise added trimethylsilyl triflate (0.37 g, 1.68 mmol) with stirring. The color of the solution turned gradually from orange to pale yellow. After 2 h stirring, the reaction mixture was allowed to slowly warm to room temperature and stirred overnight. Volatiles were removed *in vacuo*, and the residue was extracted with *n*-hexane (15 mL). Concentration and storage of the extract in a  $-20^\circ\text{C}$  freezer for 2 days afforded pale yellow crystals of **6**. Yield: 0.49 g (91%). Mp:  $206^\circ\text{C}$  (dec).  $^1\text{H}$  NMR (200.13 MHz,  $\text{C}_6\text{D}_6$ , 298 K):  $\delta$  1.09 (br, 6 H, CHMeMe), 1.12 (br, 6 H, CHMeMe), 1.13 (br, 6 H, CHMeMe), 1.16 (br, 6 H, CHMeMe), 1.62 (s, 6 H, NCMe), 3.22 (br, 4 H, CHMe<sub>2</sub>), 5.52 (s, 1 H,  $\gamma\text{-CH}$ ), 6.94–7.16 (br, 6 H, 2,6- $^i\text{Pr}_2\text{C}_6\text{H}_3$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR (50.32 MHz,  $\text{C}_6\text{D}_6$ , 298 K):  $\delta$  22.6, 23.9, 25.4, 27.9 (NC Me, CHMe); 106.0 ( $\gamma\text{-C}$ ); 124.7, 127.9, 128.5, 137.5, 140.3 (2,6- $^i\text{Pr}_2\text{C}_6\text{H}_3$ ); 167.1 (N C).  $^{19}\text{F}\{^1\text{H}\}$  NMR (188.31 MHz,  $\text{C}_6\text{D}_6$ , 298 K):  $\delta$  -77.5 ( $\text{CF}_3$ ). IR (KBr,  $\text{cm}^{-1}$ ): 627 (s), 637 (w), 761 (w), 804 (m), 936 (w), 988 (s), 1003 (w), 1030 (m), 1057 (w), 1167 (m), 1182 (s), 1190 (s), 1200 (s), 1232 (s), 1253 (m), 1260 (m), 1308 (m), 1326 (s), 1357 (s), 1385 (s), 1441 (m), 1465 (m), 1543 (s), 1586 (w), 2870 (m), 2928 (m), 2964 (s), 3062 (w), 3224 (w). Anal. Calcd for  $\text{C}_{30}\text{H}_{41}\text{N}_2\text{GeF}_3\text{SO}_3$ : C, 56.4; H, 6.5; N, 4.4. Found: C, 56.2; H, 6.9; N, 4.3. EI-MS:  $m/z$  (%) 639.3 (96,  $\text{M}^+$ ), 490.3 (93,  $[\text{M} - \text{OTf}]^+$ ), 475.2 (100,  $[\text{M} - \text{OTf} - \text{Me}]^+$ ).

**Single-Crystal X-ray Structure Determinations.** Crystals were each mounted on a glass capillary and measured in a cold  $\text{N}_2$  flow. The data were collected on a Bruker-AXS SMART CCD diffractometer at 173(2) K (Mo K $\alpha$  radiation,  $\lambda = 0.71073$  Å). The structures were solved by direct methods and were refined on  $F^2$  with the SHELX-97 software package. The positions of the H atoms were calculated and considered isotropically according to a riding model. All disordered groups were refined with distance restraints and restraints for the anisotropic displacement parameters.

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**Supporting Information Available:** CIF files giving crystallographic data for **2–6**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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