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Reactivity of Germylene toward Phosphorus-Containing Compounds: Nucleophilic Addition and Tautomerism

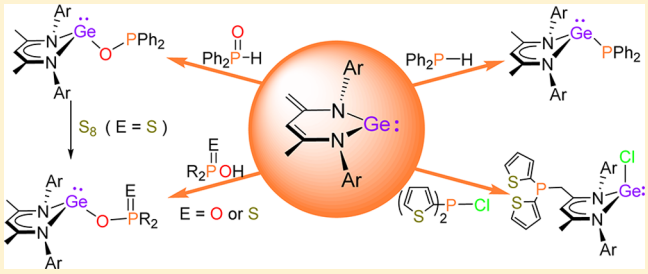
Yile Wu,[†] Liu Liu,[†] Jue Su,[†] Kaili Yan,[†] Tao Wang,[†] Jun Zhu,[‡] Xiang Gao,[§] Yuxing Gao,*[,†] and Yufen Zhao[†]

[†]Department of Chemistry and Key Laboratory for Chemical Biology of Fujian Province, College of Chemistry and Chemical Engineering, and [‡]State Key Laboratory of Physical Chemistry of Solid Surfaces and Fujian Provincial Key Laboratory of Theoretical and Computational Chemistry, College of Chemistry and Chemical Engineering, Xiamen University, Xiamen 361005, Fujian, China

[§]School of Pharmaceutical Sciences, Xiamen University, Xiamen 361102, Fujian, China

Supporting Information

ABSTRACT: A series of phosphorus-substituted germanium(II) complexes, L^1GeR [L^1 = CH{(CMe)(2,6-^{i}Pr$_2$C$_6$H$_3$N)}$_2$; **2**, R = PPh_2; **4**, R = $OPPh_2$; **5a**, R = $OP(O)Ph_2$; **5b**, R = OP(O) (O^nBu)$_2$; **6a**, R = $OP(S)Ph_2$; **6b**, R = OP(S)(OEt)$_2$], were synthesized through the direct activation of various organic phosphorus compounds by N-heterocyclic ylide-like germylene **1**. These compounds were characterized by IR and NMR spectroscopy, and **4**, **5a**, **6a**, and **6b** were further investigated by X-ray crystallography. Interestingly, the reaction of **1** with $Ph_2P(O)H$ produced the tricoordinated phosphorus(III) species $L^1GeOPPh_2$ (**4**) rather than the expected isomeric product $L^1GeP(O)Ph_2$. The reaction of **1** with dialkylthiophosphoric acid and diphenylthiophosphinic acid resulted in the products **6a** and **6b** containing the P═S double bond rather than the P═O double bond.



INTRODUCTION

Stable heavier group 14 element carbene analogues have received much attention over the years.[1] Because of the dual Lewis acid/base character properties, germylenes show high reactivity that they can form donor−acceptor bonds with transition metals,[2] participate as ligands in some organic reactions,[3] add to unsaturated substrates[4] or be coordinated by carbenes.[5] Besides, germylene plays key roles in the facile activation of small molecules and functional groups. Power et al.[6] and Jones et al.[7] demonstrated that [R^1GeGeR^1] [R^1 = C_6H_3-2,6(C_6H_3-2,6-^{i}Pr$_2$)$_2$], [(R^2)GeGe(R^2)] [R^2 = N(SiMe$_3$)(Ar^1); Ar^1 = C_6H_2Me{C(H)Ph_2}$_2$-4,2,6], [$GeAr^2_2$] [Ar^2 = C_6H_3-2,6-(C_6H_2-2,4,6-Me$_3$)$_2$], and [$SnAr^2_2$]-activated H_2 or P_4. Several groups reported that germanium(II) hydride [L^1GeH] [L^1 = CH{(CMe)(2,6-^{i}Pr$_2$C$_6$H$_3$N)}$_2$] acted as an effective reagent to activate CO_2[8] and ketones.[9] Furthermore, a catalytic amount of germanium(II) hydride also promoted the hydroboration reaction via the activation of ketone.[10] The activation of aldehydes using germanium(II) cyanides [(L^2)GeCN] (L^2 = aminotroponiminate) and isocyanate using germanium(II) alkoxides [L^1GeO^iPr] was revealed by Siwatch and Nagendran[11] and Fulton et al.,[12] respectively, which indicated that germanium(II) complexes might be potential catalysts for organic reactions. In 2006, Driess and co-workers first demonstrated a new type of N-heterocyclic ylide-like germylene **1** that was capable of activating halohydrocarbon,[13] ammonia,[14] water, phenol, and carboxylic acid.[15] Note that **1** activated the C−H bond of alkynes and produced alkynyl/alkenyl-substituted germylenes.[16]

Phosphorus-containing organometallic complexes have widespread applications in modern synthesis chemistry,[17] and they can also be used as precursors to coordinate with other metal atoms.[18] To date, the most common method for the synthesis of phosphorus-substituted germanium(II) complexes was a salt elimination reaction;[19] however, the method heavily suffered from poor scope of the phosphorus-containing substrate and the requirement of previous preparation of moisture-sensitive P−Li substrates through the reaction of P−Cl or P−H compounds with metal lithium. We wondered if it might have access to these compounds in a one-step process, directly using commercial available organic phosphorus compounds as starting materials and avoiding the use of a highly active P−Li reagent. Hence, we focused our endeavors toward the direct activation of various readily obtainable phosphorus-containing compounds by germylene through a relatively simple route (Scheme 1). In this paper, we demonstrated the reactivity of N-heterocyclic germylene **1** toward various phosphorus compounds, which results in the direct 1,4-addition products **2**, **3**, **4**, **5a**, **4b**, **6a**, and **6b** as well as the intramolecular interconvertible products **4**, **6a**, and **6b**.

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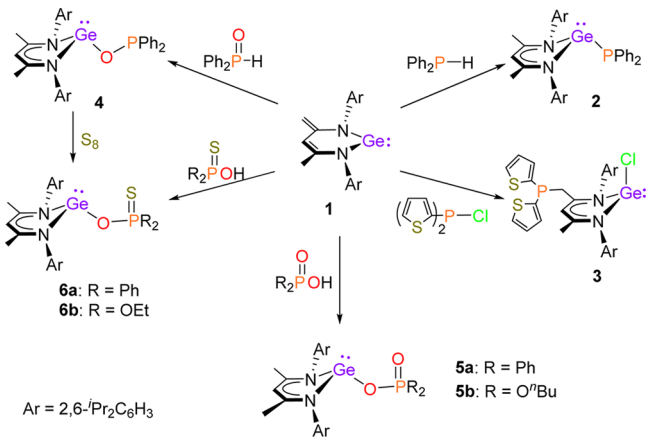
Scheme 1. Activation of Phosphorus-Containing Compounds by N-Heterocyclic Ylide-like Germylene 1



RESULTS AND DISCUSSION

Germylenes are germanium analogues of carbenes and silylenes. Since the discovery of the first isolable germylenes (R_2Ge) reported by Lappert et al.,[20] a variety of stable germylenes have been prepared. Among them, the planar N-heterocyclic germylene **1** is simply accessible by treating [L^1GeCl] with 1 equiv of $LiN(SiMe_3)_2$ at room temperature[13] or by treating [L^1GeCl] with 1 equiv of N-heterocyclic carbene (1,3-di-*tert*-butylimidazol-2-ylidene).[14] To gain more insight into the electronic properties of **1**, density functional theory (DFT) calculations were carried out. On the basis of natural resonance theory (NRT) calculations (M06-2X/TZVP), this germylene is mainly described as a dipolar resonance hybrid (Figure 1a),

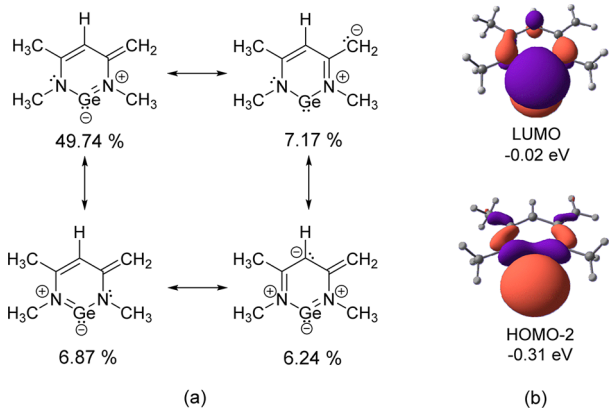


Figure 1. Major resonance structures and molecular orbitals (isovalue = 0.04) of the N-heterocyclic germylene.

where the germanium possesses one lone pair of electrons. The interaction of both nitrogen lone pairs and the germanium vacant orbital of the germylene gives rise to a polarized allylic system, which could further stabilize the electron-deficient Ge center. The HOMO−2 and LUMO of the germylene (Figure 1b) show one lone pair of electrons and an empty p orbital in Ge, respectively, and thus react both as Lewis base and Lewis acid.

Because the stable carbenes or silylenes can cleave the P−H bond at a single C center or at a Si center,[21] the germylene should be able to activate the P−H bond. The mixture of **1** and diphenylphosphine (Ph_2PH) was dissolved in toluene and heated in a sealed tube at 100 °C for 12 h, resulting in the generation of $LGePPh_2$ (**2**; Scheme 2).[19a] **2** was further characterized by NMR, electrospray ionization mass spectrometry (ESI-MS), and IR. Selected ^{1}H and ^{31}P NMR chemical shifts are listed in Table 1.

Scheme 2. Reaction of 1 toward Ph_2PH

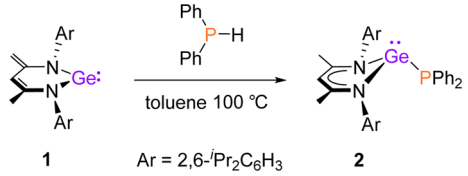


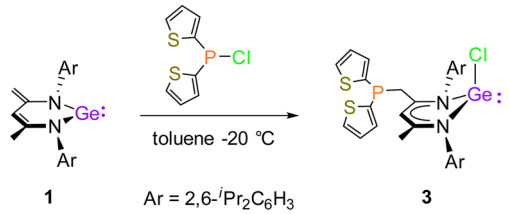
Table 1. Selected ^{31}P and ^{1}H NMR Chemical Shifts for Compounds 2, 3, 4, 5a, 5b, 6a, and 6b

compound	^{31}P NMR[b] (δ, ppm)[a]	^{1}H NMR (γ-C*H*; δ, ppm)[a]
2	−36.09	4.75
3	−39.96	5.03[b]
4	96.59	5.11
5a	19.90	5.44
5b	−3.89	5.12
6a	66.86	5.21
6b	61.31	4.87

[a]The NMR data were collected with the solvent C_6D_6. [b]Doublet.

Inspired by the results above and the work reported previously,[22] we introduced phosphorus substituent groups into the ligand backbone. The reaction of **1** with (2-thienyl)$_2$PCl at −20 °C produced pale-yellow crystals of **3** in a nearly quantitative yield (Scheme 3). **3** was further

Scheme 3. Reaction of 1 toward (2-Thienyl)$_2$PCl



characterized by NMR, ESI-MS, IR, and single-crystal X-ray studies. In the molecule of **3** (Figure 2), one thienyl ring linked to the P atom is disordered over two positions with unequal populations for each orientation (the ratio of the occupancies is 2.89:1).

For both dialkyl phosphonates and secondary phosphine oxides, there is a tautomeric equilibrium between tri- and tetracoordinated forms in the solution state. The tricoordinated form is favored in the presence of a Lewis base.[23] Although H-phosphonates and phosphine oxides are widely used as efficient phosphorylating reagents in C−P and N−P bond formation,[24] most of the phosphorylated products are in a tetracoordinated form. Besides, little attention has been paid to their applications in the phosphorylation of organometallic compounds, especially the germanium(II) compounds.

A toluene solution of 1 equiv of **1** and 1 equiv of diphenylphosphine oxide [$Ph_2P(O)H$] was heated at 100 °C. The color of the solution changed gradually from dark red to yellow. After 6 h of heating, the solvent was removed and a small amount of *n*-hexane was added in, resulting in pale-yellow

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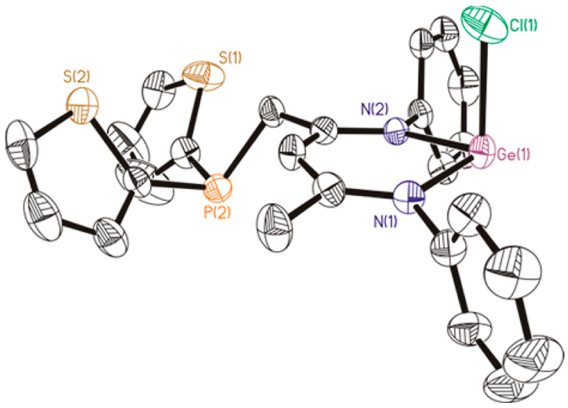
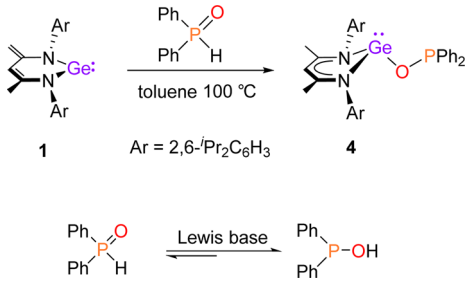


Figure 2. Molecular structure of **3** with the anisotropic displacement parameters depicted at the 50% probability level. The H atoms, isopropyl groups, and disorder on one of the thienyl rings linked to P(2) atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Ge(1)−N(1) 1.9737(17), Ge(1)−N(2) 1.9913(17), Ge(1)−Cl(1) 2.3017(9); N(1)−Ge(1)−N(2) 91.30(7), N(1)−Ge(1)−Cl(1) 95.98(6), N(2)−Ge(1)−Cl(1) 94.46(5).

microcrystalline solid **4** (Scheme 4). ^{31}P NMR analysis of **4** revealed a high-field singlet (δ 96.59 ppm), the characteristic

Scheme 4. Reaction of 1 toward $Ph_2P(O)H$

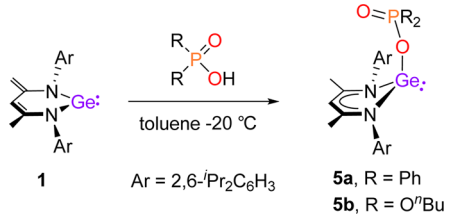


peak of tricoordinated phosphine complexes. The ^{1}H NMR spectrum of **4** exhibited a singlet at δ 5.11 ppm, corresponding to γ-C*H* of the ligand backbone.

Yellow block crystals were obtained by growing the above pale-yellow microcrystalline solid in a *n*-hexane solution at −20 °C for 2 days. The resulting crystals were examined by X-ray structural analysis. The molecular structure of compound **4** is shown in Figure 3. In contrast to Ph_2PH, $Ph_2P(O)H$ underwent intramolecular tautomerism during the reaction, producing the tricoordinated phosphorus germanium(II) complex **4**. The six-membered C_3N_2Ge ring of **4** exhibits a boatlike conformation, and the lone pair of electrons on the P atom is on the same side as the Ge atom. The Ge−O bond length [1.875(3) Å] is slightly longer than that found in L^{1}GeOH [1.828(1) Å],[25] L^{1}GeOPh [1.860(4) Å],[15a] and L^{1}GeO^{i}Pr [1.821(2) Å].[12] Importantly, the HOMO and HOMO−1 of **4** are mainly localized at the p orbitals of the Ge and P atoms (Figure 3, right), respectively, showing that **4** is a rare example of a bidentate ligand that contains both Ge and P as coordinating atoms.

Treatment of **1** with diphenylphosphinic acid [$Ph_2P(O)OH$] in toluene at −20 °C led to an immediate color change of the resulting solution from dark red to light yellow. With the addition of *n*-hexane, white solid **5a** was precipitated from the solution (Scheme 5). The ^{31}P NMR spectrum of **5a** displays a

Scheme 5. Reaction of 1 toward $R_2P(O)OH$



singlet (δ 19.90 ppm) that is close to those in [(thf)$_3$Ca(O$_2$PPh$_2$)I]$_2$ (δ 17.1 ppm)[19c] and [Pd(Phen)(OP(O)Ph$_2$)$_2$] (δ 30.7 ppm).[26] The ligand backbone γ-C*H* of **5a** displays a singlet at δ 5.44 ppm in the ^{1}H NMR spectrum.

Compound **5a** crystallized from a mixture of *n*-hexane and toluene in a ratio of 3:1. The molecular structure of **5a** (Figure 4) features a Ge−O−P angle of [149.24(15)°], the signal of which is wider than that in **4** [114.75(16)°]. The Ge−O bond length [1.919(2) Å] is longer than that in **4** and is shorter than that of LGeOC$_6$F$_5$ [1.9515(14) Å].[15a] The P(1)−O(1) bond that is nearly parallel to the N(1)−Ge(1) bond has a bond length of [1.482(2) Å], distinctly shorter than that of the P(1)−O(2) single bond [1.548(2) Å].

Similarly, the reaction of **1** with dibutyl phosphate [(^{n}BuO)$_2$P(O)OH] afforded yellow crystals of **5b** (Scheme 5) but in a low yield of 36%. The ^{31}P NMR spectrum of **5b** displays a singlet at δ −3.89 ppm, which is close to that of the starting material (^{n}BuO)$_2$P(O)OH. The singlet at δ 5.12 ppm in the ^{1}H NMR spectrum is identified as the ligand backbone γ-C*H* of **5b**. In addition to **5b**, a small amount of colorless crystals was isolated from the reaction mixture after 4 days at

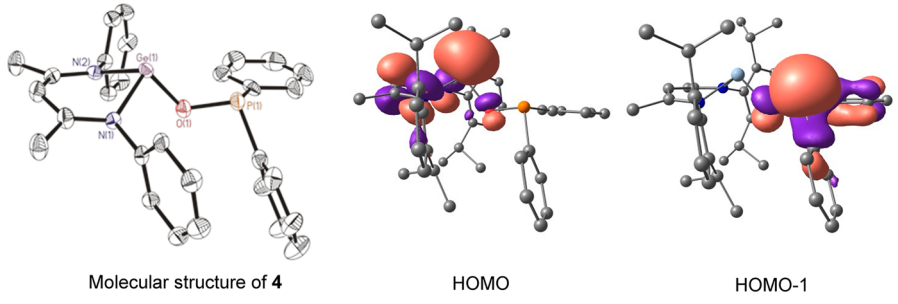


Figure 3. Molecular structure of **4** with the anisotropic displacement parameters depicted at the 50% probability level. The H atoms and isopropyl groups have been omitted for clarity. Selected bond lengths (Å) and angles (deg): Ge(1)−N(1) 2.006(4), Ge(1)−N(2) 2.018(4), Ge(1)−O(1) 1.875(3), P(1)−O(1) 1.631(3); N(1)−Ge(1)−N(2) 88.76(15), N(1)−Ge(1)−O(1) 97.39(13), N(2)−Ge(1)−O(2) 95.70(13), Ge(1)−O(1)−P(1) 114.75(16). HOMO and HOMO−1 (isovalue = 0.04) of **4**.

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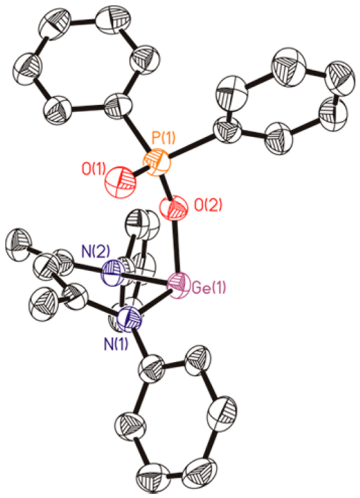
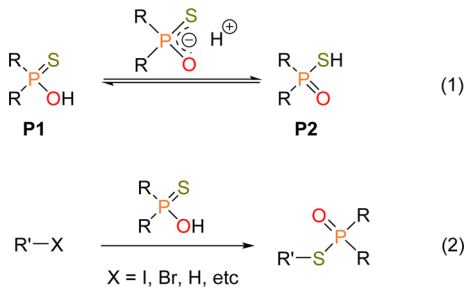


Figure 4. Molecular structure of **5a** with the anisotropic displacement parameters depicted at the 50% probability level. The H atoms and isopropyl groups have been omitted for clarity. Selected bond lengths (Å) and angles (deg): Ge(1)−N(1) 1.965(3), Ge(1)−N(2) 1.986(3), Ge(1)−O(2) 1.919(2), P(1)−O(1) 1.482(2), P(1)−O(2) 1.548(2); N(1)−Ge(1)−N(2) 90.98(11), N(1)−Ge(1)−O(2) 95.23(10), N(2)−Ge(1)−O(2) 90.44(11), Ge(1)−O(2)−P(1) 149.24 (15), O(1)−P(1)−O(2) 118.02(14).

−20 °C, which was proven to be the ligand L^1H by ^1H and ^{13}C NMR. However, when $Ph_2P(O)OK$ [prepared by the reaction of 1 equiv of $Ph_2P(O)OH$ with 1 equiv of KOH] was used as the phosphorus source, the reaction of L^1GeCl with $Ph_2P(O)$-OK gave no desired product **5a**. This indicates that the addition of $R_2P(O)OH$ to **1** is an efficient approach to synthesizing complexes with the Ge−O−P═O moiety. Unfortunately, the reaction of **1** with phenylphosphinic acid [$PhP(O)(OH)_2$] at −78 °C only produced almost quantitative L^1H.

Dialkylthiophosphoric acids and diphenylthiophosphinic acid are important intermediates in synthesis chemistry.[27] Both of them have tautomeric equilibrium between the P═S double bond form (**P1**) and the P═O double bond form (**P2**) [Scheme 6, eq 1].[28] Moreover, the gas-phase free energies of

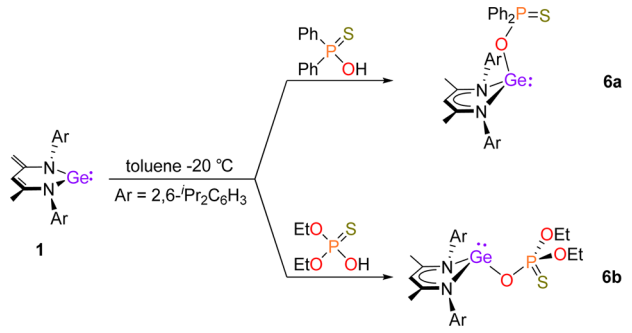
Scheme 6. Tautomerism of $R_2P(S)OH$



$(EtO)_2P(O)SH$ and $Ph_2P(O)SH$ are 8.8 and 10.8 kcal/mol higher than those of $(EtO)_2P(S)OH$ and $Ph_2P(S)OH$ at the M06-2X/SVP level, respectively. Indeed, it has been reported that the diphenylthiophosphinic acid [$Ph_2P(S)OH$] exhibits the **P1** form in a solid state.[29] However, most of the reactions using diethylthiophosphoric acid [$(EtO)_2P(S)OH$] as the starting material led to the products with P═O double bonds (Scheme 6, eq 2).[27] The ^{31}P NMR spectrum of $(EtO)_2P(S)OH$ displays a low-field singlet at δ 58.0 ppm,[27c] indicating that this compound should be the **P1** form.

The reaction of **1** with $Ph_2P(S)OH$ at −20 °C produced pale-yellow crystalline solids **6a** in high yield (Scheme 7).

Scheme 7. Reaction of 1 toward $R_2P(S)OH$



Compound **6a** has a characteristic band (632.6 cm^{-1}) in the IR spectrum, demonstrating the presence of the P═S double bond. The DFT calculations show the vibrational frequency of the P═S double bond in **6a** is 637.8 cm^{-1} at the M06-2X/SVP level. Comparable IR bands are found in $Ph_3GeOP(S)Me_2$ (617 cm^{-1}),[28d] $Ph_3GeOP(S)Ph_2$ (660 cm^{-1}),[30] and $Ph_2P(S)$-OMe (635 cm^{-1}).[30] The ^{31}P NMR spectrum of **6a** displays a singlet at δ 66.86 ppm and the ^1H NMR spectrum γ-C*H* of the ligand backbone at δ 5.21 ppm.

The pale-yellow crystal of **6a** was obtained after a mixture of **6a**, *n*-hexane, and toluene was reserved at −20 °C for 12 h (Figure 5). In the molecular structure of **6a**, the P(1)−S(1) double bond length [1.9380(8) Å] is distinctly longer than that of the P−O double bond in **4a** and close to that the P−S double bond found in $Ph_2P(S)OH$.[29] Furthermore, the Ge−O−P [143.24(9)°] and O−P−S [118.41(6)°] angles in **6a** are close to the Ge−O−P and O−P−O angles found in **4a**, respectively. Interestingly, because the S atom is located on the same side of the lone-pair electrons of the Ge^{II} center, **6a** might be a fascinating class of bidentate ligands.

The mixing of $(EtO)_2P(S)OH$ with **1** in the solution of toluene at −20 °C led to a yellow solution (Scheme 7), from which colorless crystalline **6b** was isolated. The structure and constitution of compound **6b** were characterized by elemental analysis, ^1H, ^{31}P, and ^{13}C NMR spectroscopy, and single-crystal X-ray diffraction analysis (Figure 5). Interestingly, in contrast to most of the C−S-bond-containing products starting with $(EtO)_2P(S)OH$ (Scheme 6, eq 2), **6b** exists as a product having Ge−O and P═S group moieties rather than the one containing Ge−S and P═O group moieties. Moreover, the S atom in **6b** is located on the reverse side of the lone-pair electrons of the Ge^{II} center, which is significantly different from that in **6a**. In addition, the two O atoms on the ethoxyl groups are aligned with the Ge atom, creating a bowllike chelating environment, which makes **6b** a potentially useful tridentate ligand.

Although it is well-known that the Ge^{II} and P^{III} atoms can be oxidized by elemental S,[8,31] little attention has been focused on the oxidation of Ge^{II} and P^{III} in one compound by elemental S. Therefore, we introduced elemental S as an oxidant for **4** to evaluate the reducing power of Ge^{II} and P^{III}. The reaction of 1 equiv of **4** with $^1/_8$ equiv of S_8 only produced the phosphorus-oxidized product **6a** (isolated yield, 81%; in situ ^{31}P NMR yield, >99%), whereas the Ge center remained divalent (Scheme 8). This result indicates that, in compound **4**, the tricoordinated P^{III} atom is more readily oxidized than the tricoordinated Ge^{II}

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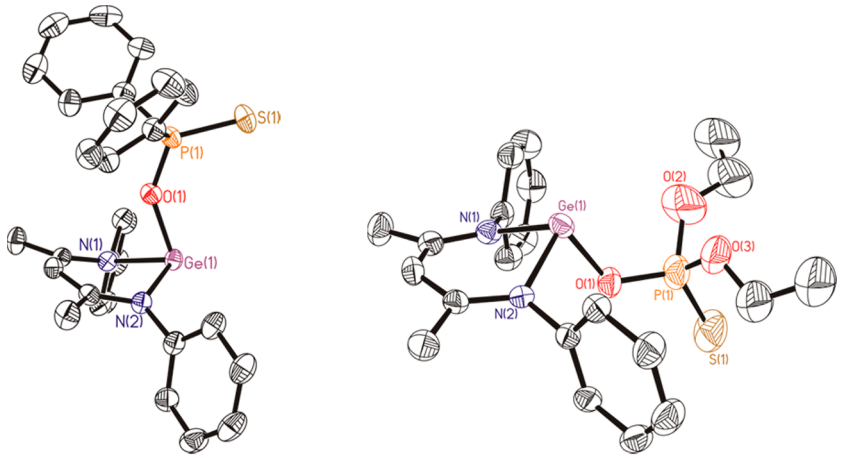
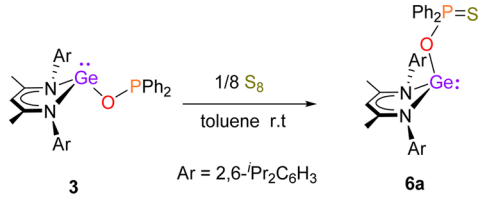


6a 6b

Figure 5. Molecular structures of **6a** and **6b** with the anisotropic displacement parameters depicted at the 50% probability level. The H atoms, isopropyl groups, one lattice solvent molecule (toluene) of **6a**, and disorder on the ethoxyl groups linked to P(1) atoms in **6b** have been omitted for clarity. Selected bond lengths (Å) and angles (deg): (1) for **6a**, Ge(1)−O(1) 1.9303(14), Ge(1)−N(2) 1.9750(16), Ge(1)−N(1) 1.9773(16), O(1)−P(1) 1.5369(14), P(1)−S(1) 1.9380(8); N(2)−Ge(1)−N(1) 89.89(7), N(1)−Ge(1)−O(1) 88.94(6), N(2)−Ge(1)−O(1) 90.31(6), P(1)−O(1)−Ge(1) 143.24(9), O(1)−P(1)−S(1) 118.41(6); (2) for **6b**, Ge(1)−O(1) 1.897(3), Ge(1)−N(1) 1.972(4), Ge(1)−N(2) 1.974(3), P(1)−O(1) 1.507(3), P(1)−S(1) 1.905(2); N(1)−Ge(1)−N(2) 88.92(14), O(1)−P(1)−S(1) 116.37(17).

Scheme 8. Reaction of 4 with S_8



atom. It is reasonable that the P^{III} atom is oxidized upon treatment with sulfur, whereas the Ge^{II} atom remains intact because the s character of the lone pair on the Ge atom is more than that of the P atom.

CONCLUSIONS

With this work, we first systematically investigated the reactivity of N-heterocyclic ylide-like germylene **1** toward a variety of readily available and stable organic phosphorus compounds. These valuable phosphorus-containing germanium(II) complexes, L^1GeR (L^1 = CH[C(Me)N(Ar)]$_2$; Ar = 2,6-^{i}Pr$_2$C$_6$H$_3$; R = phosphorus-containing substituent groups), could be conveniently obtained in a one-pot process. As one of its notable features, germylene **1** exhibits good compatibility with various types of phosphorus substrates and allows them to be reacted efficiently, such as H-phosphine, H-phosphites, phosphinic acids, phosphate esters, thiophosphoric acids, and thiophosphinic acids. Most interestly, the reaction of **1** with $Ph_2P(O)H$ only afforded tricoordinated phosphorus (Ph_2PO)-substituted product **4** rather than tetracoordinated phosphorus [$Ph_2P(O)$]-substituted product. These reactions above represented a new route to the direct activation of multifarious phosphorus compounds by germylene, and these products contain P, O, and S atoms in one molecule in addition to the Ge^{II} center, which make them potential chelating ligands.

COMPUTATIONAL DETAILS

Calculations were carried out with the *Gaussian 09* package.[32] Geometry optimizations were performed with the M06-2X functional.[33] The TZVP[34] basis set was used for the calculation in Figure 1. Frequency calculations at the same level of theory were performed to identify the number of imaginary frequencies (zero for the local minimum) and to provide the frontier molecular orbitals (HOMO and LUMO). NRT calculations were carried out using the *NBO 5.9* program[35] at the M06-2X/TZVP level. The SVP[34] basis set was used for calculations of $(EtO)_2P(O)SH$, $Ph_2P(O)SH$, $(EtO)_2P(S)OH$, $Ph_2P(S)OH$, **4**, and **6a**. The Cartesian coordinates are provided in the Supporting Information (SI).

EXPERIMENTAL SECTION

General Procedures. All manipulations were carried out on a Schlenk line or in an inert-atmosphere glovebox. Solvents were dried by refluxing with sodium benzophenone under N_2, distilled, and stored over 3 Å sieves. N-Heterocyclic ylide-like germylene **1**[13] and (2-thienyl)$_2$PCl[36] were prepared according to procedures reported in the literature. $R_2P(S)OH$ were prepared by treating the relevant $R_2P(O)H$ with S_8 and Et_3N in a solution of diethyl ether. Unless otherwise stated, commercial reagents were purchased from Aldrich or Acros and used without further purification. ^{1}H, ^{31}P, and ^{13}C NMR spectra were recorded on a Bruker AV 400 or a Bruker AV 500 spectrometer. ^{1}H and ^{13}C NMR spectroscopic chemical shifts were given relative to residual solvent peaks, and the ^{31}P NMR chemical shifts were externally referenced to 85% H_3PO_4. IR spectra were recorded on a Nicolet 330 spectrometer.

*L^1GePPh_2 (**2**).* A mixture of Ph_2PH (0.372 g, 2 mmol) and **1** (0.978 g, 2 mmol) in toluene (10 mL) was heated at 100 °C in a sealed tube. After 12 h, the solvent was removed under vacuum, 10 mL of *n*-hexane was added, and red crude crystalline powders were obtained. The red powders were washed by cooled *n*-hexane (2 × 2 mL), and the residues were dried in a vacuum to afford pure **2** (0.95 g, 70%). ^{1}H NMR (500 MHz, C_6D_6, ppm): δ 7.03−6.96 (m, 8 H, Ar*H*), 6.86−6.81 (m, 4 H, Ar*H*), 6.79−6.76 (m, 4 H, Ar*H*), 4.74 (s, 1 H, γ-H), 4.16−4.12 (m, 2 H, C*H*Me$_2$), 3.24 (sept, J = 6.8 Hz, 2 H, C*H*Me$_2$), 1.70 (d, J = 6.8 Hz, 6 H, CH*Me*$_2$), 1.45 (s, 6 H, β-Me), 1.21 (d, J = 6.9 Hz, 6 H, CH*Me*$_2$), 1.08 (d, J = 6.9 Hz, 6 H, CH*Me*$_2$), 0.98 (d, J = 6.8 Hz, 6 H, CH*Me*$_2$). ^{13}C{^{1}H} NMR (125 MHz, C_6D_6, ppm): δ 167.03 (*C*N), 145.31, 143.49, 141.59 (Ar), 141.08 (d, J_{C-P} = 28.1 Hz, Ar), 135.70 (d, J_{C-P} = 16.8 Hz, Ar), 128.29, 127.33, 125.25, 124.55 (Ar), 97.31 (γ-*C*H), 29.33, 29.26 (*C*HMe$_2$), 28.73, 25.51, 25.24, 24.80, 24.40 (CH*Me*$_2$), 24.34 (CH*Me*$_2$), 22.92 (β-Me). ^{31}P NMR (202 MHz, C_6D_6, ppm): δ −36.09. IR (Nujol mull, cm^{-1}): $\tilde{\nu}$ 1553.0, 1513.0, 1317.8,

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1250.6, 1176.9, 1023.4, 933.8, 852.1, 794.5, 757.7, 736.9, 695.3, 500.1. ESI-MS: m/z 677 ($[M + H]^+$). Elem. anal. Calcd for $C_{41}H_{51}GeN_2P$: C, 72.90; H, 7.61; N, 4.15. Found: C, 72.78; H, 7.69; N, 4.29.

*(2-Thienyl)$_2$PLGeCl (**3**).* To a cooled (−20 °C) solution of **1** (0.489 g, 1 mmol) in toluene (20 mL) was added a solution of (2-thienyl)$_2$PCl (0.233 g, 1 mmol) in toluene (10 mL). The solution quickly turned yellow while the mixture was slowly brought to room temperature. After the mixture was stirred for 12 h, toluene was removed and 5 mL of cooled *n*-hexane was added. The yellow precipitate **3** was dried under vacuum (0.58 g, 80%). ^{1}H NMR (400 MHz, C_6D_6, ppm): δ 7.28 (ddd, J = 6.6, 3.5, and 1.1 Hz, 1 H, thienyl-*H*), 7.18−7.04 (m, 7 H, Ar*H*), 7.01 (dd, J = 4.9 and 1.1 Hz, 1 H, thienyl-*H*), 6.90 (dd, J = 4.9 and 1.1 Hz, 1 H, thienyl-*H*), 6.62 (ddd, J = 4.9, 3.5, and 1.3 Hz, 1 H, thienyl-*H*), 6.55 (ddd, J = 4.9, 3.5, and 1.3 Hz, 1 H, thienyl-*H*), 5.03 (d, J = 1.6 Hz, 1 H, γ-H), 3.99 (sept, J = 6.7 Hz, 1 H, C*H*Me$_2$, overlapped), 3.93 (sept, J = 6.7 Hz, 1 H, C*H*Me$_2$, overlapped), 3.35 (sept, J = 6.7 Hz, 1 H, C*H*Me$_2$, overlapped), 3.38−3.26 (m, 2 H, PCH_2, overlapped), 1.51 (d, J = 6.6 Hz, 3 H, CHMe_2), 1.48 (s, 3 H, β-Me, overlapped), 1.47 (d, J = 6.8 Hz, 3 H, CHMe_2, overlapped), 1.40 (d, J = 6.8 Hz, 3 H, CHMe_2), 1.31 (d, J = 6.8 Hz, 3 H, CHMe_2), 1.28 (d, J = 6.8 Hz, 3 H, CHMe_2, overlapped), 1.27 (d, J = 6.8 Hz, 3 H, CHMe_2, overlapped), 1.16 (d, J = 6.8 Hz, 3 H, CHMe_2), 1.09 (d, J = 6.8 Hz, 3 H, CHMe_2). ^{13}C{^{1}H} NMR (100 MHz, C_6D_6, ppm): δ 165.40 (CN), 163.14 (d, J_{C-P} = 11.1 Hz, NCCH$_2$P), 147.18, 144.71, 143.70, 139.40 (d, J_{C-P} = 105.8 Hz, thienyl), 139.38, 139.05, 138.96, 138.67 (Ar), 136.74 (d, J_{C-P} = 30.4 Hz, thienyl), 134.96 (d, J_{C-P} = 27.1 Hz, thienyl), 131.79 (d, J_{C-P} = 113.7 Hz, thienyl), 128.13, 127.87 (Ar), 125.56 (d, J = 2.2 Hz, Ar), 124.67, 124.03 (Ar), 101.33 (d, J = 8.5 Hz, γ-CH), 40.62 (d, J_{C-P} = 17.1 Hz, CH_2P), 29.40, 29.18, 28.66, 28.30, 28.14, 27.71 (CHMe$_2$ and CHMe_2), 26.50 (β-Me), 24.92, 24.88, 24.80, 24.50, 24.24, 24.01, 23.43 (CHMe$_2$ and CHMe_2). ^{31}P NMR (162 MHz, C_6D_6, ppm): δ −39.96. IR (Nujol mull, cm^{-1}): $\tilde{\nu}$ 1584.9, 1532.1, 1313.5, 1287.8, 1250.6, 1203.4, 1169.2, 1117.7, 990.5, 930.5, 793.4, 759.1, 721.9, 699.1, 574.8, 424.7. ESI-MS: m/z 723 ($[M + H]^+$). Elem. anal. Calcd for $C_{33}H_{46}ClGeN_2PS_2$: C, 61.56; H, 6.42; N, 3.88. Found: C, 61.43; H, 6.29; N, 3.76.

*L^{1}GeOPPh$_2$ (**4**).* A mixture of Ph$_2$P(O)H (0.404 g, 2 mmol) and **1** (0.978 g, 2 mmol) in toluene (10 mL) was heated at 100 °C in a sealed tube, and the color changed from dark red to yellow in the next 6 h. After the solvent was removed, about 10 mL of *n*-hexane was added, resulting in the formation of yellow crystalline solid **4** (0.70 g, 67%). A *n*-hexane solution of **4** was kept at −20 °C for 2 days to obtain the yellow block crystals **4** ready for X-ray analysis. ^{1}H NMR (500 MHz, C_6D_6, ppm): δ 7.36−7.34 (m, 4 H, Ar*H*), 7.19−7.16 (m, 2 H, Ar*H*), 7.14−7.12 (m, 2 H, Ar*H*), 7.10−7.05 (m, 8 H, Ar*H*), 5.10 (s, 1 H, γ-H), 3.62−3.57 (m, 2 H, C*H*Me$_2$), 3.20 (sept, J = 6.8 Hz, 2 H, C*H*Me$_2$), 1.61 (s, 6 H, β-Me), 1.22 (d, J = 6.8 Hz, 6 H, CHMe_2), 1.18 (d, J = 6.8 Hz, 6 H, CHMe_2), 1.13 (d, J = 6.8 Hz, 6 H, CHMe_2), 1.00 (d, J = 6.8 Hz, 6 H, CHMe_2). ^{13}C{^{1}H} NMR (125 MHz, C_6D_6, ppm): δ 164.65 (CN), 147.62 (d, J_{C-P} = 27.4 Hz, Ar), 146.32, 144.89, 140.63 (Ar), 132.15 (d, J_{C-P} = 22.4 Hz, Ar), 128.69, 128.49, 127.90 125.63, 124.85 (Ar), 100.58 (γ-CH), 29.27 (CHMe$_2$), 28.88, 28.85 (CHMe$_2$), 26.32, 26.10 (CHMe_2), 24.99, 24.93 (CHMe_2), 23.20 (β-Me). ^{31}P NMR (202 MHz, C_6D_6, ppm): δ 96.59. IR (Nujol mull, cm^{-1}): $\tilde{\nu}$ 1553.9, 1522.8, 1460.7, 1440.5, 1375.2, 1364.3, 1319.3, 1263.3, 1174.8, 1021.0, 935.5, 822.1, 791.0, 739.7, 691.5, 584.3, 472.5. ESI-MS: m/z 693 ($[M + H]^+$). Elem. anal. Calcd for $C_{41}H_{51}GeN_2OP$: C, 71.22; H, 7.43; N, 4.05. Found: C, 71.35; H, 7.29; N, 4.09.

*L^{1}GeOP(O)Ph$_2$ (**5a**).* At −20 °C, a suspension of Ph$_2$P(O)OH (0.219 g, 1 mmol) in toluene (15 mL) was added drop by drop to a solution of **1** (0.489 g, 1 mmol) in toluene (20 mL). The mixture was stirred and slowly warmed to room temperature. After the solvent was stirred for an additional 12 h, it was removed and *n*-hexane was added to get white crystalline solid **5a** (0.42 g, 59%). The solution of **5a** in *n*-hexane/toluene (2:1) was stored at −20 °C for 1 day, and colorless block crystals of **5a** suitable for X-ray testing were obtained. ^{1}H NMR (500 MHz, C_6D_6, ppm): δ 7.82−7.77 (m, 4 H, Ar*H*), 7.19−7.11 (m, 5 H, Ar*H*), 7.09−7.06 (m, 7 H, Ar*H*), 5.44 (s, 1 H, γ-H), 3.53 (sept, J = 6.8 Hz, 2 H, C*H*Me$_2$), 3.11 (sept, J = 6.8 Hz, 2 H, C*H*Me$_2$), 1.78 (s, 6 H, β-Me), 1.16 (d, J = 6.9 Hz, 6 H, CHMe_2), 1.12 (d, J = 6.1 Hz, 3 H, CHMe_2, overlapped), 1.11 (d, J = 6.2 Hz, 3 H, CHMe_2, overlapped), 0.95 (d, J = 6.7 Hz, 6 H, CHMe_2). ^{13}C{^{1}H} NMR (125 MHz, C_6D_6, ppm): δ 165.08 (CN), 146.06, 144.36, 139.59 (Ar), 138.54 (d, J_{C-P} = 134.9 Hz, Ar), 131.83 (d, J_{C-P} = 9.5 Hz, Ar), 129.85 (d, J_{C-P} = 2.5 Hz, Ar), 127.79 (d, J_{C-P} = 48.4 Hz, Ar), 127.39, 125.03, 124.10 (Ar), 101.99 (γ-CH), 28.59, 28.01 (CHMe$_2$), 25.62, 25.39, 24.28, 24.10 (CHMe_2), 22.92 (β-Me). ^{31}P NMR (202 MHz, C_6D_6, ppm): δ 19.90. IR (Nujol mull, cm^{-1}): $\tilde{\nu}$ 1521.9, 1314.9, 1255.4, 1206.8, 1126.8, 1111.1, 1003.0, 973.2, 858.7, 797.6, 780.3, 722.3, 695.7, 546.8, 505.9, 419.8. ESI-MS: m/z 709 ($[M + H]^+$). Elem. anal. Calcd for $C_{41}H_{51}GeN_2O_2P$: C, 69.61; H, 7.27; N, 3.96. Found: C, 69.74; H, 7.15; N, 4.04.

*L^{1}GeOP(O)(O^{n}Bu)$_2$ (**5b**).* A solution of (^{n}BuO)$_2$P(O)OH (0.210 g, 1 mmol) in toluene (10 mL) was added dropwise to a solution of **1** (0.489 g, 1 mmol) in toluene (20 mL) at −20 °C. The resulting mixture was stirred and slowly warmed to room temperature. After 3 h, the solvent was removed, and the residues were extracted by 15 mL of *n*-hexane. The extract was stored at −20 °C for 12 h to get yellow crystalline solid **5b** (0.25 g, 36%). The filtrate was further stored at −20 °C for 6 days, from which colorless crystals L^{1}H were isolated (0.09 g, 22% yield based on **1**). ^{1}H NMR (500 MHz, C_6D_6, ppm): δ 7.26−7.06 (m, 6 H, Ar*H*), 5.12 (s, 1 H, γ-H), 3.98 (sept, J = 6.8 Hz, 2 H, C*H*Me$_2$), 3.90−3.85 (m, 2 H, OCH_2), 3.73−3.70 (m, 2 H, OCH_2), 3.12 (sept, J = 6.8 Hz, 2 H, C*H*Me$_2$), 1.65 (s, 6 H, β-Me), 1.60 (d, J = 6.8 Hz, 6 H, CHMe_2), 1.37 (d, J = 6.8 Hz, 6 H, CHMe_2), 1.29−1.22 (m 10 H, CHMe_2 and OCH$_2$CH_2), 1.10 (d, J = 6.8 Hz, 6 H, CHMe_2), 0.83 (t, J = 7.4 Hz, 6 H, CH$_2$*Me*). ^{13}C{^{1}H} NMR (125 MHz, C_6D_6, ppm): δ 164.84 (CN), 146.89, 144.34, 139.52, 128.29, 125.30 (Ar), 100.56 (γ-CH), 65.52 (d, J_{C-P} = 5.4 Hz, OCH_2), 33.19 (d, J_{C-P} = 7.1 Hz, OCH$_2$CH_2), 29.02, 28.17, (CHMe$_2$), 26.28, 25.71, 24.82, 24.56 (CHMe_2), 23.11 (β-Me), 19.21 (CH$_2$Me), 13.90 (CH$_2$*Me*). ^{31}P NMR (202 MHz, C_6D_6, ppm): δ −3.89. IR (Nujol mull, cm^{-1}): $\tilde{\nu}$ 1620.7, 1553.7, 1517.2, 1320.5, 1249.0, 1171.8, 1047.9, 1004.2, 897.8, 856.9, 794.3, 757.8, 727.2, 517.3, 440.1. ESI-MS: m/z 723 ($[M + Na]^+$). Elem. anal. Calcd for $C_{37}H_{59}GeN_2O_4P$: C, 63.65; H, 8.50; N, 4.00. Found: C, 63.51; H, 8.71; N, 4.13.

*L^{1}GeOP(S)Ph$_2$ (**6a**).* A solution of Ph$_2$P(S)OH (0.234 g, 1 mmol) in toluene (10 mL) was added dropwise to a solution of **1** (0.489 g, 1 mmol) in toluene (20 mL) at −20 °C. The resulting mixture was stirred and slowly warmed to room temperature. The solvent was removed 12 h later, and the residues were extracted with *n*-hexane (2 × 2 mL). The residual pale-yellow crystalline solid was proven to be **6a** (0.640 g, 89%). The solution of **6a** in *n*-hexane/toluene (1:1) was stored at −20 °C for an additional 12 h, and pale-yellow block crystals of **6a** suitable for X-ray testing were obtained. ^{1}H NMR (500 MHz, C_6D_6, ppm): δ 7.86−7.82 (m, 4 H, Ar*H*), 7.18−7.15 (m, 2 H, Ar*H*), 7.10−7.07 (m, 4 H, Ar*H*), 7.00−6.99 (m, 6 H, Ar*H*), 5.21 (s, 1 H, γ-H), 3.44 (sept, J = 6.8 Hz, 2 H, C*H*Me$_2$), 3.12 (sept, J = 6.8 Hz, 2 H, C*H*Me$_2$), 1.66 (s, 6 H, β-Me), 1.21 (d, J = 6.8 Hz, 6 H, CHMe_2), 1.15 (d, J = 6.8 Hz, 6 H, CHMe_2), 1.12 (d, J = 6.8 Hz, 6 H, CHMe_2), 0.81 (d, J = 6.8 Hz, 6 H, CHMe_2). ^{13}C{^{1}H} NMR (125 MHz, C_6D_6, ppm): δ 165.51 (CN), 145.83 (d, J_{C-P} = 107.2 Hz, Ar), 142.38, 141.52, 140.46 (Ar), 132.28 (d, J_{C-P} = 11.1 Hz, Ar), 130.54 (d, J_{C-P} = 2.6 Hz, Ar), 128.91, 128.51, 125.85, 125.34 (Ar), 101.36 (γ-CH), 29.66, 29.25 (C*H*Me$_2$), 26.65, 26.58, 25.26, 25.00 (CHMe_2), 23.80 (β-Me). ^{31}P NMR (202 MHz, C_6D_6, ppm): δ 66.86. IR (Nujol mull, cm^{-1}): $\tilde{\nu}$ 1304.9, 1193.9, 1177.4, 1132.7, 1078.0, 972.0, 924.0, 854.5, 796.5, 723.7, 632.6, 617.7, 513.4. ESI-MS: m/z 725 ($[M + H]^+$). Elem. anal. Calcd for $C_{41}H_{51}GeN_2OPS$: C, 68.06; H, 7.11; N, 3.87. Found: C, 68.29; H, 7.23; N, 3.85.

*L^{1}GeOP(S)(OEt)$_2$ (**6b**).* A solution of (EtO)$_2$P(S)OH (0.170 g, 1 mmol) in toluene (10 mL) was added dropwise to a solution of **1** (0.489 g, 1 mmol) in toluene (20 mL) at −20 °C. The resulting mixture was stirred and slowly warmed to room temperature. After the solvent was stirred for an additional 12 h, it was removed, and the residual yellow solid was washed by cooled *n*-hexane (2 × 2 mL). The residues were dried under vacuum to afford analytically pure **6b** (0.47 g, 71%).^{1}H NMR (400 MHz, C_6D_6, ppm): δ 7.20−7.04 (m, 6 H, Ar*H*), 4.87 (s, 1 H, γ-H), 3.84 (m, 4 H, OCH_2 and C*H*Me$_2$), 3.90−3.85 (m, 2 H, OCH_2), 3.39−3.38 (m, 2 H, OCH_2), 3.20−3.16 (m, 2

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H, CHMe$_2$), 1.60 (d, J = 6.6 Hz, 6 H, CHMe$_2$), 1.54 (s, 6 H, β-Me), 1.37 (d, J = 6.6 Hz, 6 H, CHMe$_2$), 1.25 (d, J = 6.5 Hz, 6 H, CHMe$_2$), 1.19 (dd, J = 21.6 and 6.9 Hz, 6 H, CH$_2$Me), 1.11 (d, J = 6.5 Hz, 6 H, CHMe$_2$). ^{13}C{^{1}H} NMR (100 MHz, C$_6$D$_6$, ppm): δ 164.49 (CN), 146.07, 144.59, 138.87, 127.62, 125.00, 124.52 (Ar), 98.62 (γ-CH), 62.15 (OCH$_2$), 29.12, 28.53 (CHMe$_2$), 26.17, 25.52, 25.00, 24.68 (CHMe$_2$), 22.74 (β-Me), 16.12 (d, J = 8.8 Hz, CH$_2$Me$_2$). ^{31}P NMR (162 MHz, C$_6$D$_6$, ppm): δ 61.31. IR (Nujol mull, cm^{-1}): $\tilde{\nu}$ 1551.6, 1523.4, 1491.9, 1316.5, 1250.2, 1172.4, 1097.9, 1039.9, 1018.4, 980.3, 948.9, 854.5, 793.2, 756.8, 746.9, 718.7, 629.3, 510.1, 440.5. ESI-MS: m/z 683 ([M + Na]$^+$). Elem. anal. Calcd for $C_{33}H_{51}GeN_2O_3PS$: C, 60.11; H, 7.80; N, 4.25. Found: C, 60.17; H, 7.63; N, 4.38.

X-ray Crystallographic Analysis. X-ray structural data were collected on a Bruker Smart APEX diffractometer with Mo Kα (λ = 0.71073 Å) radiation and a CCD area detector. The *SHELX*, version 6.1, program package was used for structure solutions (*SHELXS-97*)[37] and refinements (*SHELXL-97*).[38] Cell parameters, data collection, structure solution, and refinement details are given in Table 1s in the SI.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Crystallographic tables, CIF files, ^{1}H, ^{31}P, and ^{13}C NMR spectra, and Cartesian coordinates. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: gaoxingchem@xmu.edu.cn.

Notes

The authors declare no competing financial interest.

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