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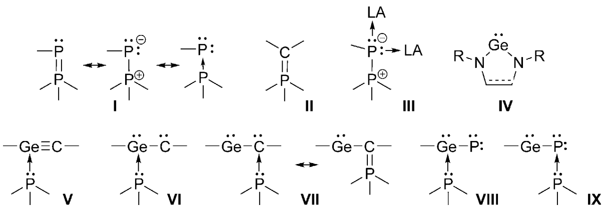
A Stable Heterocyclic Amino(phosphanylidene-σ^4-phosphorane) Germylene

Natalia Del Rio, Antoine Baceiredo, Nathalie Saffon-Merceron, Daisuke Hashizume, Dennis Lutters, Thomas Müller, and Tsuyoshi Kato**

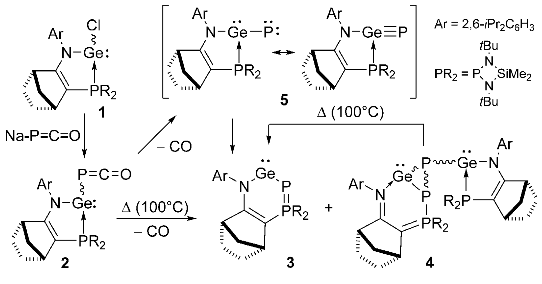
Abstract: *A new stable heterocyclic germylene, in which the divalent germanium atom lies between a nitrogen atom and a phosphanylidene phosphorane group, was synthesized. Experimental and theoretical studies revealed the peculiar effect of phosphanylidene phosphorane substituent, which is a stronger π-donor towards germanium than an amino group is. Because of the weak phosphorus–germanium π-bond, this new germylene compound shows an enhanced reactivity compared to classical N-heterocyclic germylenes.*

As represented by N-heterocyclic carbenes (NHCs),[1] stable divalent species of group 14 elements have become important chemical tools in various research domains.[2,3] It is obvious that the development of new substituent systems, which allow precise control of the properties, such as donor–acceptor character and their stability, is the key to this chemistry. Particularly strong π-donating substituents, such as amino groups, considerably modify the singlet–triplet energy gap of these species, thus leading to an improved stability.[4] Although amino groups are most frequently used to stabilize divalent species, other strongly π-donating substituents, such as chalcogenolate[5,6] phosphino,[7,8] and phosphonium ylide[9–11] groups, have also demonstrated their efficiency. However, the number of available π-donating substituents remains limited.

A potentially interesting new π-donating substituent is the phosphanylidene phosphorane **I**, which is the phosphorus analogue of a phosphonium ylide. Similar to Wittig reagents (**II**), **I** presents a highly polarized P═P bond and thus should be strong π donors. Indeed, preliminary studies on the few known stable compounds[12–14] have clearly demonstrated the great potential of **I**, which can be regarded as a phosphine-stabilized phosphinidene, as a strong σ-donating ligand (**III**).[15] However, their use as a stabilizing electron-donating substituent has not yet been described.[16] Herein, we report the synthesis of a new stable heterocyclic germylene **3** (for structure see Scheme 1) with an enhanced reactivity compared to the well-known, but moderately reactive N-heterocyclic germylenes (NHGe) **IV**,[17] The high reactivity of **3** can be related to the peculiar substituent effect of the phosphanylidene phosphorane fragment compared to classical amino substituents.



Recently, we reported the synthesis of the first isolable germyne (-Ge≡C-) stabilized by a phosphine ligand (**V**), which can also be regarded as an α,α′-bis(carbenoid) species (**VI**) featuring a carbene center and a phosphine-stabilized germylene fragment.[11] This molecule isomerizes at room temperature by a 1,2-migration of the phosphine ligand from the germanium to the carbon center to give the stabilized phosphonium-ylide-substituted germylene **VII**. Following a similar synthetic strategy, instead of **VI**, we considered the generation of the phosphinidene derivative **VIII**, whose rearrangement should give the expected phosphanylidene-phosphorane-substituted germylene of type **IX**. For this purpose, we chose the germylene substituted phosphaketene **2** as a phosphinidene precursor (Scheme 1).[18] Derivative **2** was synthesized by the reaction of the phosphine-stabilized chloro(amino)germylene **1** with one equivalent of sodium



Scheme 1. Synthesis and thermolysis of the phosphaketene-functionalized germylene **2**.

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[*] N. Del Rio, Dr. A. Baceiredo, Dr. T. Kato
Université de Toulouse, UPS, and CNRS, LHFA UMR 5069
118 route de Narbonne, 31062 Toulouse cedex 9 (France)
E-mail: kato@chimie.ups-tlse.fr
Homepage: http://hfa.ups-tlse.fr

M. Sc. D. Lutters, Prof. Dr. T. Müller
Institut für Chemie
Carl von Ossietzky Universität Oldenburg
Carl von Ossietzky-Strasse 9–11, 26111 Oldenburg (Germany)

Dr. D. Hashizume
Materials Characterization Support Unit
RIKEN Center for Emergent Matter Science (CEMS)
Wako, Saitama 351-0198 (Japan)

Dr. N. Saffon-Merceron
Université de Toulouse, UPS, ICT-FR2599
118 route de Narbonne, 31062 Toulouse cedex 9 (France)

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phosphaethynolate,[19] which was recently developed by the group of Grützmacher as a convenient P-transfer reagent, and **2** was isolated in good yield as yellow crystals (71 %). The phosphaketene **2** was obtained as a mixture of two diastereomers (80:20) as indicated by the two AX-systems in ^{31}P NMR spectroscopy (major isomer: $\delta = -317.3$ and 90.7 ppm, $^2J_{pp} = 32.4$ Hz, minor isomer: $\delta = -315.9$ and 90.1 ppm, $^2J_{pp} = 34.9$ Hz). An intense IR absorption band at 1920 cm^{-1} is in agreement with the presence of a phosphaketene function. The structure of **2** was unambiguously confirmed by an X-ray diffraction analysis (Figure 1).[20] The molecular structure of **2** is similar to previously reported structures of phosphine-stabilized germylenes.[11,21]

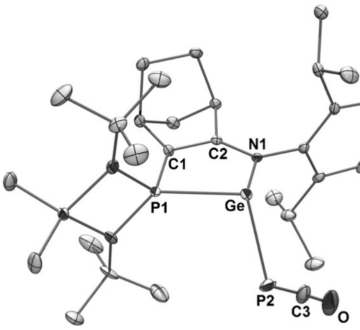


Figure 1. Molecular structure of **2**. Thermal ellipsoids represent 30% probability. H atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Ge-N1 1.988(4), Ge-P2 2.4329(8), Ge-P1 2.497(3), P2-C3 1.670(4), P1-C1 1.716(4), C1-O 1.167(4), C2-N1 1.355(2), C1-C2 1.387(3), P1-Ge-P2 99.66(7), Ge-P2-C3 86.01(12), P2-C3-O 178.0(3), Ge-P1-C1 94.13(14), P1-C1-C2 117.76(17), C1-C2-N1 126.6(3), C2-N1-Ge 115.7(3).

The phosphaketene **2** is thermally unstable, and the release of carbon monoxide starts around 80 °C in toluene. The reaction was monitored by ^{31}P NMR spectroscopy, thus indicating the complete disappearance of **2** after 3 hours at 100 °C (Scheme 1). Neither the phosphinidene- nor phosphagermyne-type intermediate **5** were observed during the reaction. Instead, the thermolysis of **2** led to the clean formation of the heterocyclic germylene **3** (70 %) and the unsymmetrical dimer **4** (30 %). Both **3** and **4** are perfectly stable in solution at room temperature. However, **4** slowly decomposes at 100 °C into **3**, and after additional heating (3 h at 100 °C then 1 h at 130 °C), **3** was obtained as a unique product.

The heterocyclic germylene **3** was successfully isolated as yellow crystals, from a heptane solution at room temperature, in 40 % yield. The presence of two phosphorus atoms is clearly indicated by an AX-system in the ^{31}P NMR spectrum ($\delta = 111.1$ and 52.4 ppm, $^1J_{pp} = 550.6$ Hz), and the large J_{pp} coupling constant is in agreement with directly connected phosphorus atoms. The low-field chemical shift ($\delta = 111.1$ ppm) for the dicoordinated phosphorus atom suggests a P–Ge multiple bond character (**A**; see Figure 3), even though phosphagermenes usually appear at lower field ($\delta = 175$–416 ppm).[22] Indeed, in the case of a phosphanylidene structure (resonance structure **B**), the chemical shift for the

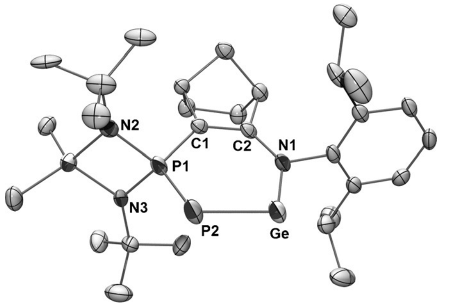


Figure 2. Molecular structure of **3**. Thermal ellipsoids represent 30% probability. H and disordered atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Ge-N1 1.918(4), Ge-P2 2.247(2), P2-P1 2.095(2), P1-C1 1.744(6), C1-C2 1.376(8), C2-N1 1.374(6); N1-Ge-P2 107.0(2), Ge-P2-P1 105.6(1), P2-P1-C1 114.3(2), C2-N1-Ge 129.4(4), P1-C1-C2 129.2(5), C1-C2-N1 130.5(6).

divalent phosphorus atom would be expected at much higher field.[23] The X-ray diffraction analysis of **3** (Figure 2) confirms this bonding situation. Indeed, the Ge–P2 distance in **3** [2.247(2) Å] is significantly shorter than the previously reported Ge^{II}–P distances (ca. 2.38 Å),[24] and is very similar to the distance observed in the bis(phosphino) germylene [(Dipp$_2$P)$_2$Ge:], featuring a trigonal planar P atom (Ge–P: 2.234 and 2.382 Å).[8] This bond length is in agreement with a strong π-donation of the phosphanylidene phosphorane fragment, and with a significant Ge–P multiple bond character in **3** (resonance structure **A**). The observed P1–P2 bond length of 2.095(2) Å is consistent with a P–P multiple bond character and is even shorter than those in phosphanylidene phosphoranes (2.141–2.184 Å; **B** in Figure 3).[12–14] Of particular interest, the Ge-N1 bond length [1.918(4) Å] is significantly longer than those observed in cyclic diamino germylenes (1.80–1.86 Å),[17,25] thus suggesting little contribution of resonance structure **C** (π-interaction of the amino group with the divalent Ge center). However, the essentially planar geometry around N1 ($\Sigma°$N1 = 358.17°) indicates certain π-electron delocalization of the nitrogen lone pair toward the Ge^{II} atom as well as C2=C1−P1 fragment.

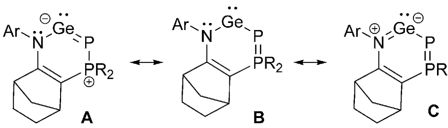


Figure 3. Some possible resonance structures of **3**.

The unsymmetrical structure of **4**, having four different phosphorus atoms, was indicated by the ^{31}P NMR spectrum, and since **4** exists as a mixture of four diastereomers (proportions: 47:42:8:3), four systems were observed. One of those isomers was isolated as colorless crystals, from a heptane solution at room temperature, in 59 % yield and its structure was confirmed by an X-ray diffraction analysis (Figure 4). The structure of **4** shows two units of the monomer featuring two different donor-stabilized germylene centers. The first one (Ge2) presents a phosphine-stabilized germy-

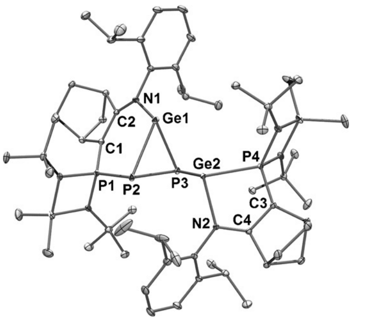
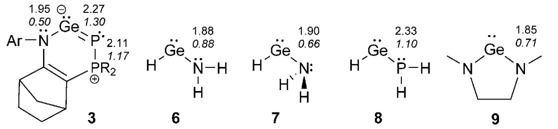


Figure 4. Molecular structure of **4**. Thermal ellipsoids represent 30% probability. H atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Ge1-N1 2.0063(6), Ge1-P2 2.4373(2), Ge1-P3 2.4330(2), P2-P3 2.2193(3), P2-P1 2.1434(3), Ge2-P3 2.3869(2), P1-C1 1.7244(8), C1-C2 1.3903(12), C2-N1 1.3350(14), Ge2-N2 2.0027(6), Ge2-P4 2.4126(2), P4-C3 1.7312(7), C3-C4 1.3918(11), C4-N2 1.3427(9); P2-Ge1-P3 54.218(7), Ge1-P2-P3 62.792(8), Ge1-P3-P2 62.991(8), Ge1-P2-P1 102.060(10), Ge1-P3-Ge2 79.904(7), P1-P2-P3 104.578(11), P2-P3-Ge2 84.078(9), N1-Ge1-P3 99.24(2), N1-Ge1-P2 104.01(2), P3-Ge2-N2 106.16(2), P3-Ge2-P4 104.949(7), N2-Ge2-P4 85.285(19).

lene whose geometry is very similar to that of the germylenes **1** and phosphaketene **2** (Scheme 1). The second one (Ge1) is a three-membered cyclic diphosphinogermylene in which Ge^{II} is stabilized by the intramolecular coordination of the imine fragment. Recently, we reported a related structure of a donor-stabilized silacyclopropylidene[26] and it presents a unique reactivity resulting from the strained small cyclic structure.[27] An original NHC-stabilized germacyclopropylidene was also recently described.[28] Of particular interest, the molecular structure of **4** shows unusually small Ge1-P3-Ge2 [89.904(7)°] and P2-P3-Ge2 [84.078(9)°] angles, and very short interatomic distances (Ge1-Ge2: 3.10 Å, P2-Ge2: 3.09 Å). The interatomic distances are shorter than the sum of the van der Waals radii (Ge–Ge: 4.6 Å, P–Ge: 4.1 Å), thus suggesting the presence of the interactions between either Ge1 and Ge2 or P2 and Ge2. Although experimental electron density analysis from X-ray diffraction as well as the results of QTAIM analysis for **4** did not indicate covalent bonding between Ge1 and Ge2, the calculations indicate the presence of relatively strong dispersion interactions in **4** (87 kJ mol^{-1}, see the Supporting Information for details). These interactions enforce a conformation of the dimer which brings both Ge atoms and P2 into close proximity, and results in small but significant calculated Wiberg bond indices for both linkages ($WBI_{Ge1\text{-}Ge2} = 0.14$, $WBI_{Ge2\text{-}P2} = 0.20$). The conclusions drawn from our model calculations, which are presented in the Supporting Information, indicate that the large aryl and alkyl substituents force the Ge and P atoms to approach closely, and are responsible for these relatively large dispersion force energies.[29–31]

Although the mechanism of the reaction is still obscure, formally, **4** can be rationalized as a [2+1] cycloadduct between the transient **5** (Scheme 1) and **3**. Both processes, the formation of **3** from **5** (by 154 kJ mol^{-1}) as well as the subsequent cycloaddition reaction to give **4**, are calculated to be exothermic by 256 kJ mol^{-1}, at the M06-2X/6-311 + G(d,p) level of theory. From these data the following reaction course seems to be plausible: the first formed intermediate after CO elimination is **5**, which rearranges to form **3**. With excess **5** still available **4** is formed and serves as a room-temperature stable reservoir for both types of monomers. Upon entropy-driven thermal decomposition of the dimer, both monomers are regenerated and the exothermic rearrangement of **5** to **3** is driven to completion (see the Supporting Information for a detailed discussion of the entropy effects on the equilibrium between **3**, **5**, and **4**).

To gain more information about **3**, DFT calculations were performed at the M06-2X/6-311 + G(d,p) level of theory.[32,33] The calculated molecular structure of **3** is consistent with the experimental data. The results of the structure calculations also strongly indicate the predominance of the canonical structures **A** and **B** with only minor contributions from the structure **C** (Figure 3). In detail, the comparison of bond lengths and Wiberg bond indices (WBI)[34] for **3** and the amino- and phosphino-germylenes **6**–**8**, and for the NHGe **9** indicate for the Ge–P and for the P–P linkages, the bond orders are between one and two (Figure 5). The Ge–N bond in **3** is even weaker than that in the conformer **7** of aminogermylene, in which the amino group is oriented perpendicular to the HGeN plane.[35] This bonding situation is reflected also in the frontier molecular orbitals (FMO) of **3** (Figure 6), in particular when compared to those of **9**. The FMOs of NHGe **9**, an example for cyclic diaminogermylenes, are of π symmetry, which is typical for heteroallylic three-center-4π-electron systems. In marked contrast, in the case of **3** the FMOs are mainly localized at the Ge–P linkage. The highest occupied molecular orbital (HOMO) corresponds to the π bond between Ge and the dicoordinated P atom, without significant contributions from the N atom, and the LUMO is its antibonding counterpart (Figure 6). This data suggests that the phosphanylidene phosphorane fragment is a stronger π donor towards the divalent Ge than the amino group is (considered to be one of the strongest π-donating substituents). The HOMO−1 corresponds to the combination of the lone pairs at the Ge and P atoms, and parallels the situation for the HOMO−1 in **9**, which is dominated by the lone pair on Ge. The HOMO−1 energy level of **3** (−6.66 eV) is much higher than that of **9** (−8.07 eV), probably because of the electropositive P (2.2) directly connected to the Ge center instead of N (3.0) as well as to the strong π-electron donation of the phosphanylidene phosphorane substituent. More interestingly, in spite of the strong electron donation from the phosphanylidene phosphorane function, the singlet–triplet energy gap, ΔE_{ST}, of **3** (165 kJ mol^{-1}) is considerably smaller than that of the NHGe **8** (283 kJ mol^{-1}), thus implying



3 **6** **7** **8** **9**

Figure 5. Pertinent calculated bond lengths (Å) and WBIs (italic) of **3** and of the amino- and phosphino-germylenes **6**–**9** calculated at M06-2X/6-311+G(d,p).

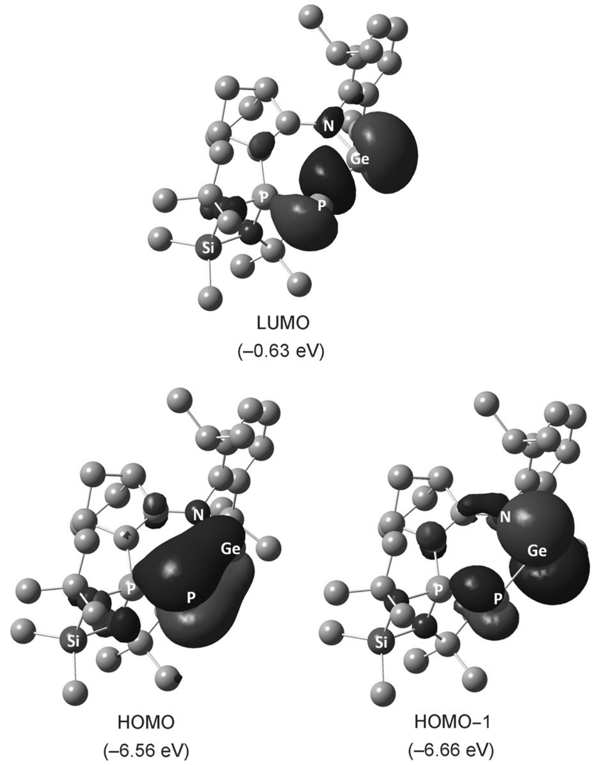


Figure 6. Surface diagrams of the front orbitals of **3** and their corresponding energy eigenvalues [calculated at M06-2X/6-311+G(d,p), isodensity value: 0.04].

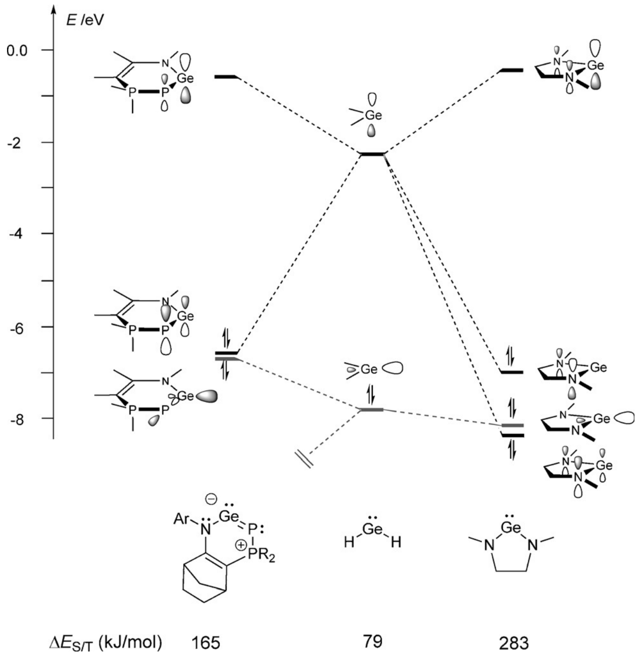
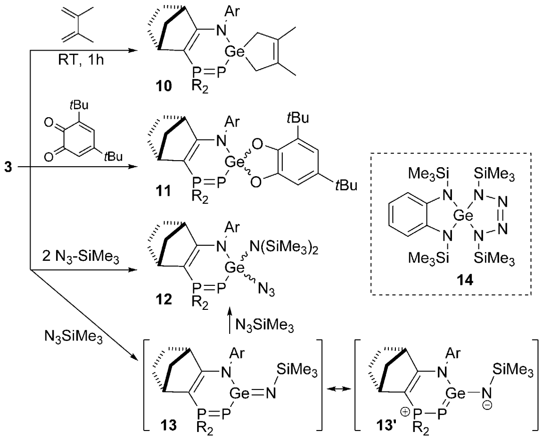


Figure 7. FMO correlation diagram of germylenes and their calculated adiabatic S/T energy differences, $\Delta E_{S/T}$.

an enhanced reactivity of **3** (Figure 7). This enhanced reactivity is probably a result of the weaker π interaction in the Ge–P link of **3** compared to the more extended and efficient allyl anion-like delocalization in **9**, as well as to the high energy level of lone pair orbital on Ge (HOMO−1).

The high reactivity of **3** was demonstrated by the reaction with 2,3-dimethylbutadiene, and it proceeds smoothly at room temperature, thus affording the corresponding [4+1] cycloadduct **10** (Scheme 2). In the ^{31}P NMR spectrum an AX-system with a large P–P coupling constant was observed [$\delta =$ −211.1 ppm (P^{II}) and 66.7 ppm (P^{IV}), $^1J_{PP} = 489.2$ Hz]. Interestingly, the P chemical shift of (P^{II}) is dramatically shifted to high-field compared to that in **3** ($\delta = 111.1$ ppm), and it appears now in the region expected for the dicoordinate P of phosphanylidene phosphoranes.[12–14] There is also a spontaneous reaction with 2,4-di-*tert*-butyl-*o*-benzoquinone at room temperature by a similar [4+1] cycloaddition process to give the germyl-substituted phosphanylidene phosphorane **11**. Two equivalents of trimethylsilylazide react with **3** at −80 °C, thus leading to the formation of the azidogermane derivative **12** (Figure 8). This reaction proceeds probably through the first formation of the germa-imine intermediate



Scheme 2. Reactivity of **3**.

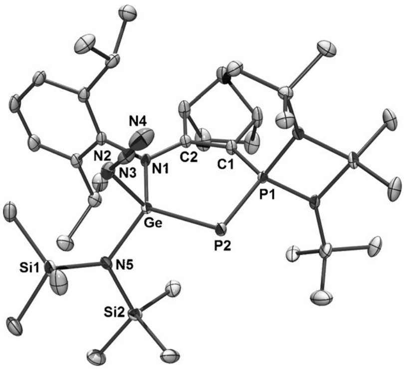


Figure 8. Molecular structure of **12**. Thermal ellipsoids represent 30% probability. H and disordered atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Ge-N1 1.890(2), Ge-N2 1.902(2), Ge-N5 1.861(2), Ge-P2 2.239(1), P2-P1 2.093(1), P1-C1 1.756(2), C2-N1 1.370(3), N2-N3 1.218(3), N3-N5 1.140(3), C1-C2 1.369(3); Ge1-N2-N3 120.1(2), N2-N3-N 174.7(2), N1-Ge-P2 116.9(1), Ge-P2-P1 100.8(1), P2-P1-C1 114.3(1), P1-C1-C2 133.4(2), C1-C2-N1 132.2(2), C2-N1-Ge 120.7(2).

13, followed by a 1,2-addition of the second equivalent of trimethylsilylazide to the Ge=N π bond. This reaction pattern is different from that observed with NHGe, which affords the tetraazagermole **14**. In this case, the first formed germa-imine intermediate probably undergoes a dipolar [3+2] cycloaddition reaction with the second equivalent of azide.[36] This behavior is different and could be rationalized by the enhanced polarization of Ge=N bond in **13,** polarization resulting from the strong π-donating phosphanylidene phosphorane fragment (**13′**), which favors the 1,2-addition versus the [3+2] cycloaddition.

In conclusion, we have synthesized a new stable P,N heterocyclic germylene (**3**) featuring a phosphanylidene phosphorane fragment, and demonstrated the peculiar electronic influence of this substituent. Indeed, the phospha-Wittig moiety appears to be a new type of electron-donating substituent, thus presenting π-donor abilities stronger than that of amino groups, and therefore capable of stabilizing electron-deficient species. Because of the weak Ge=P π bond (small π_{GeP}/ π^*_{GeP} energy gap), the singlet–triplet energy is relatively small, thus explaining why **3** is more reactive than classical NHGe. New applications of the phosphanylidene phosphorane fragment for the stabilization of other reactive species are under investigation.

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Keywords: germanium · main-group elements · multiple bonds · small-ring compounds · structure elucidation

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