Main-Group Chemistry

International Edition: DOI: 10.1002/anie.201511956
German Edition: DOI: 10.1002/ange.201511956

A Stable Heterocyclic Amino(phosphanylidene-σ⁴-phosphorane) Germylene

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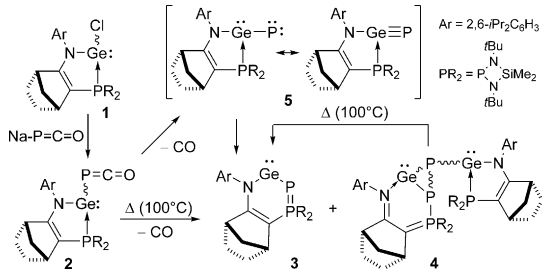
Abstract: *A new stable heterocyclic germylene, in which the divalent germanium atom lies between a nitrogen atom and a phosphanylidene phosphorane group, was synthesized. Experimental and theoretical studies revealed the peculiar effect of phosphanylidene phosphorane substituent, which is a stronger 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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Supporting information for this article can be found under: http://dx.doi.org/10.1002/anie.201511956.

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, $^{2}J_{pp} = 32.4$ Hz, minor isomer: $\delta = -315.9$ and 90.1 ppm, $^{2}J_{pp} = 34.9$ 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]

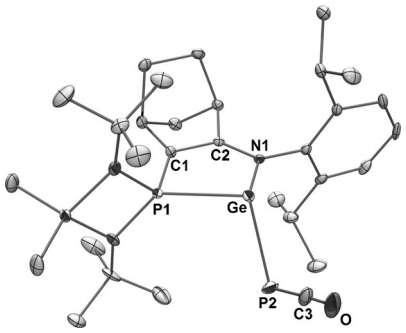


Figure 1. Molecular structure of **2**. Thermal ellipsoids represent 30% probability. H atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Ge-N1 1.988(4), Ge-P2 2.4329(8), Ge-P1 2.497(3), P2-C3 1.670(4), P1-C1 1.716(4), C1-O 1.167(4), C2-N1 1.355(2), C1-C2 1.387(3), P1-Ge-P2 99.66(7), 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, $^{1}J_{pp} = 550.6$ 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

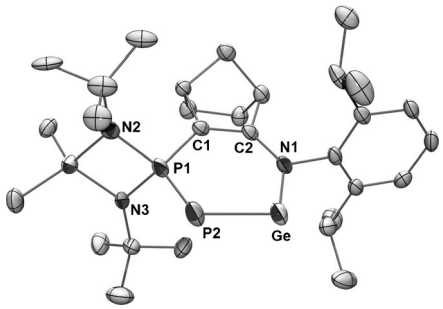


Figure 2. Molecular structure of **3**. Thermal ellipsoids represent 30% probability. H and disordered atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Ge-N1 1.918(4), Ge-P2 2.247(2), P2-P1 2.095(2), P1-C1 1.744(6), C1-C2 1.376(8), C2-N1 1.374(6); N1-Ge-P2 107.0(2), Ge-P2-P1 105.6(1),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

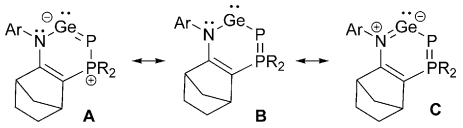


Figure 3. Some possible resonance structures of **3**.

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-

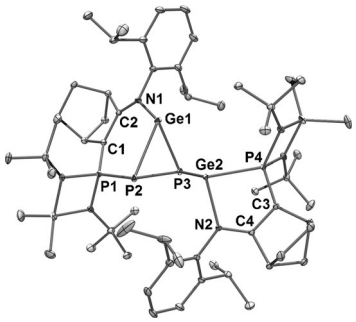


Figure 4. Molecular structure of **4**. Thermal ellipsoids represent 30% probability. H atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Ge1-N1 2.0063(6), Ge1-P2 2.4373(2), Ge1-P3 2.4330(2), P2-P3 2.2193(3), P2-P1 2.1434(3), Ge2-P3 2.3869(2), P1-C1 1.7244(8), C1-C2 1.3903(12), 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

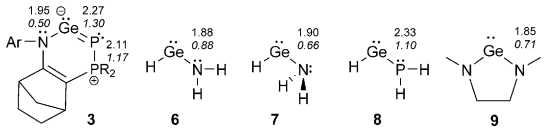


Figure 5. Pertinent calculated bond lengths (Å) and WBIs (italic) of **3** and of the amino- and phosphino-germylenes **6–9** calculated at M06-2X/6-311+G(d,p).

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

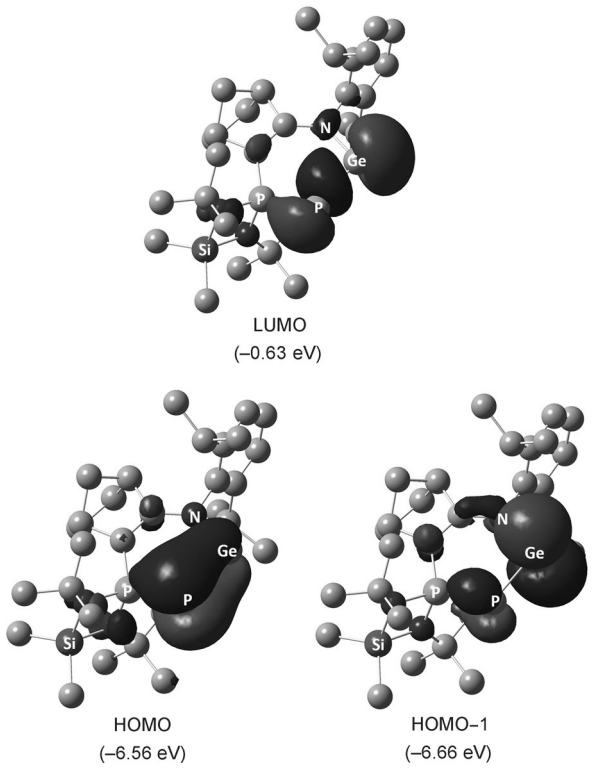


Figure 6. Surface diagrams of the front orbitals of **3** and their corresponding energy eigenvalues [calculated at M06-2X/6-311 +G(d,p), isodensity value: 0.04].

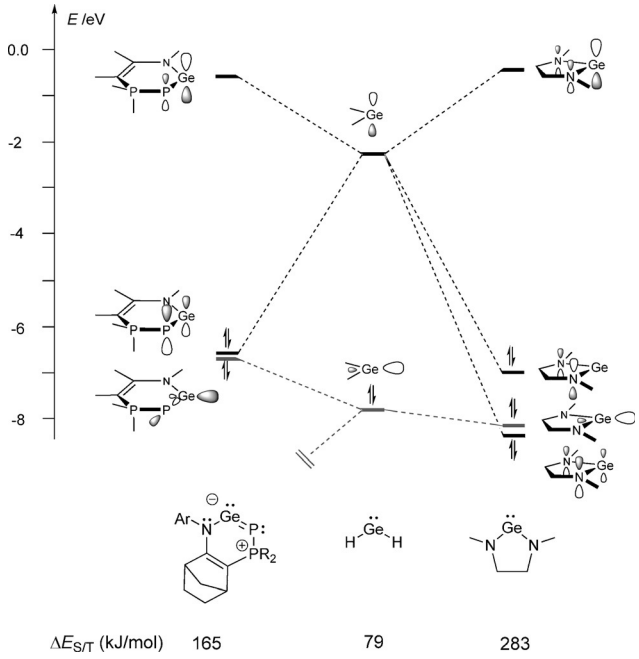
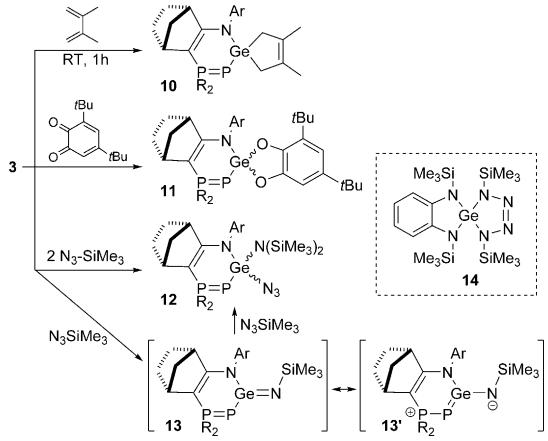


Figure 7. FMO correlation diagram of germylenes and their calculated adiabatic S/T energy differences, $\Delta E_{S/T}$.

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 [$\delta =$



Scheme 2. Reactivity of **3**.

−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

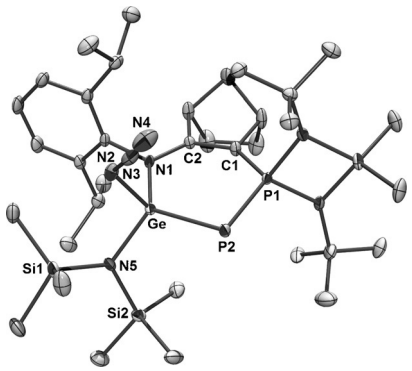


Figure 8. Molecular structure of **12**. Thermal ellipsoids represent 30% probability. H and disordered atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Ge-N1 1.890(2), Ge-N2 1.902(2), Ge-N5 1.861(2), Ge-P2 2.239(1), P2-P1 2.093(1), P1-C1 1.756(2), C2-N1 1.370(3), N2-N3 1.218(3),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

Acknowledgments

We are grateful to the CNRS, CNRS-JSPS Bilateral Joint Research Program (EDDSILICON) and the European Research Council (ERC Starting grant agreement no. 306658) for financial support of this work. The simulations were performed at the HPC Cluster HERO (High End Computing Resource Oldenburg), located at the University of Oldenburg (FRG) and funded by the DFG through its Major Research Instrumentation Programme (INST 184/108-1 FUGG) and the Ministry of Science and Culture (MWK) of the Lower Saxony State.

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

How to cite: *Angew. Chem. Int. Ed.* **2016**, *55*, 4753–4758
Angew. Chem. **2016**, *128*, 4831–4836

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Received: December 27, 2015
Revised: February 3, 2016
Published online: March 8, 2016

