

Synthesis and Reactivity of a Phosphine-Stabilized Monogermanium Analogue of Alkynes

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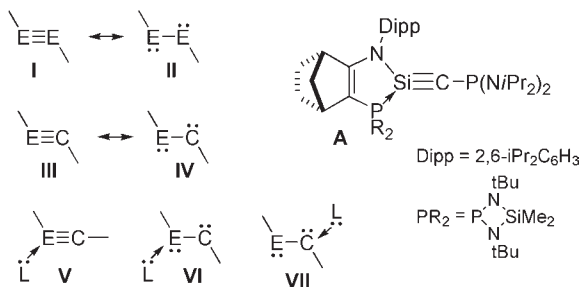
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S Supporting Information

ABSTRACT: The synthesis of the first isolable C-phosphino-Ge-aminogermynes, stabilized by a phosphine ligand, has been achieved. X-ray diffraction analysis indicates a quite long Ge–C bond whose length is between that of a single and a double bond but consistent with the theoretically predicted values for a germynes bearing π -donating substituents. The isomerization of this germynes derivative affords a new stable N-heterocyclic germynes through migration of the original phosphine ligand from germanium to the carbon center.

Carbon–carbon triple bonds are ubiquitous in organic chemistry.¹ In marked contrast, the chemistry of heavier analogues of alkynes has only recently emerged.² Indeed, the stable homonuclear alkyne analogues of the heavier group-14 elements, R–EE–R (I; E = Si–Pb), have been isolated and characterized during the past decade.^{3–6} Structural analysis of these compounds disclosed a trans-bent rather than linear geometry in which the bending angle increases in going from silicon to lead. This trend indicates increasing lone-pair character and decreasing E–E bond order (canonical structure II) upon descending the group.^{3–6} The geometrical distortion of heavier alkyne analogues relative to alkynes modifies their physical properties, leading to their unique chemical behaviors.⁷



Scheme 1. Synthesis of Phosphinogermynes 3 and Germynes 4

suggesting an increased contribution of canonical structure IV.^{10a} However, in spite of increased interest, the synthesis of stable heteronuclear alkyne analogues remains very challenging, and there have been only a few reports to date concerning the synthesis of transient species as well as theoretical investigations.^{8–11} We very recently reported the synthesis of the first isolable silyne **A** stabilized by a phosphine ligand.¹² This molecule shows a very short silicon–carbon bond that can be regarded as a silyne–base adduct with a partial Si–C triple bond (type V). The next challenge was to try to prepare the following and unknown heavier heteronuclear alkyne analogue, the germynes. Here we report the isolation and characterization of **4**, the first persistent phosphine-stabilized germynes, which have an electronic structure of type VI rather than type V, and their transformation into the thermally more stable isomers of type VII, representing new stable N-heterocyclic germynes.

By analogy with the synthesis of silyne **A**,¹² the germynes-substituted (phosphino)diazomethanes **3** were chosen as precursors of germynes. Diazomethane derivatives **3** were readily prepared by the reaction of the phosphine-stabilized chloro-(amino)germylenes **1** with lithiated phosphinodiazomethane **2**¹³ (Scheme 1) and isolated as stable orange crystalline materials [81% (**3a**), 65% (**3b**)]. **3a** was obtained as a 60:40 mixture of two diastereomers, as indicated by the two AX systems in the

In regard to the heteronuclear alkyne analogues in which one carbon atom is replaced by a heavier group-14 element, R–EC–R' (III and IV; E = Si–Pb), similar geometrical and electronic trends were theoretically predicted.^{8–11} Furthermore, Kira's group has experimentally demonstrated that a transiently formed stannylene showed a singlet-carbene-like reactivity,

Received: August 10, 2011

Published: September 13, 2011

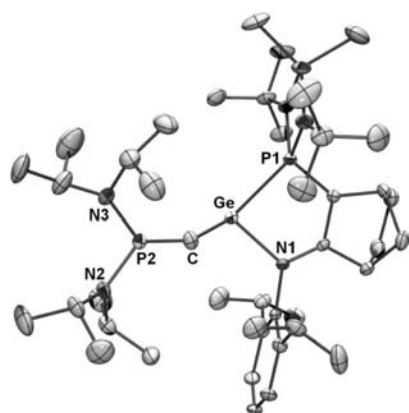


Figure 1. Molecular structure of **4a**. Thermal ellipsoids represent 30% probability. H atoms have been omitted for clarity. Selected bond lengths (Å) and angles (deg): C–Ge, 1.887(5); C–P2, 1.549(5); Ge–N1, 2.005(3); Ge–P1, 2.4895(12); P2–N3, 1.657(4); P2–N2, 1.670(4); C–Ge–N1, 102.42(18); C–Ge–P1, 113.57(14); N1–Ge–P1, 82.77(10); C–P2–N3, 126.8(2); C–P2–N2, 130.5(2); N2–P2–N3, 102.4(2); Ge–C–P2, 147.3(3). Torsion angles (deg): N2–P2–C–Ge, $-73.6(6)$; N3–P2–C–Ge, $113.9(5)$; N1–Ge–C–P2, $-159.9(5)$. $\Sigma\theta_{P2} = 359.70^\circ$, $\Sigma\theta_{Ge} = 298.76^\circ$.

^{31}P NMR spectrum [major isomer, 64.1 and 80.0 ppm ($^3J_{\text{PP}} = 91.1$ Hz); minor isomer, 64.0 and 80.9 ppm ($^3J_{\text{PP}} = 54.6$ Hz)]. An intense IR absorption band at 1995 cm^{-1} is in agreement with the presence of a diazo function. In the case of **3a**, the structure was unambiguously confirmed by X-ray diffraction (XRD) analysis.¹⁴

Photolysis of diazomethane derivatives **3** ($\lambda = 300\text{ nm}$) at -60°C in tetrahydrofuran (THF) resulted in the clean formation of the phosphine-stabilized germynes **4**. Monitoring of the reaction by ^{31}P NMR spectroscopy at -80°C showed the complete disappearance of the starting diazomethane derivative **3a** after 48 h of irradiation and the appearance of a new set of signals for **4a** [AX system: $P_{(1)} = 82\text{ ppm}$, $P_{(2)} = -20\text{ ppm}$ ($^3J_{\text{PP}} = 102.6$ Hz)], in agreement with the formation of only one diastereomer. The ^{31}P NMR data for **4a** appeared to be quite different from those of the silicon analogue **A** [AX system: $P_{(1)} = 3\text{ ppm}$, $P_{(2)} = 46\text{ ppm}$ ($^3J_{\text{PP}} = 47.3$ Hz)]. Indeed, the $P_{(2)}$ signal appeared at high field in the typical region for phosphinocarbenes,¹⁵ and the chemical shift of $P_{(1)}$ remained almost unchanged relative to the value for the starting diazo derivative **3a** (80 ppm). The ^{13}C NMR signal of the central carbon atom [162.4 ppm ($^1J_{\text{CP}} = 43.4$ Hz, $^3J_{\text{CP}} = 11.3$ Hz)] was in the region expected for a phosphinocarbene with a relatively small phosphorus–carbon coupling constant. The spectroscopic data for **4b** were very similar to those for **4a**.¹⁴

Germyne derivative **4a** was successfully isolated from diethyl ether solution at -60°C as orange crystals, and the molecular structure was confirmed by XRD analysis (Figure 1).¹⁴ This structure shows a twisted trans-bent arrangement with a N1–Ge–C–P2 dihedral angle of 159.9° and coordination of the phosphine ligand to the germanium center with a P1–Ge distance of 2.490 Å. This P1–Ge distance is slightly elongated relative to that in precursor **3a** (2.443 Å). The Ge–C bond distance (1.887 Å) is quite long in comparison with the calculated value for a Ge–C triple bond in the parent compound (1.73 Å)⁹ and lies between the lengths of a single (1.98 Å)¹⁶ and a double bond (1.80 Å).² However, this bond distance is consistent with

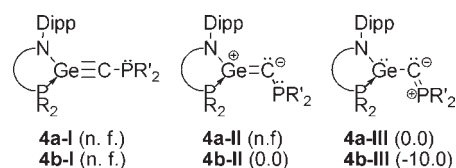


Figure 2. Possible structures for **4a** and **4b**. Relative energies (kcal/mol) calculated at the BHandH/6-31G* level of theory are given in parentheses. Structures **4a-I**, **4b-I**, and **4a-II** were not found (n.f.).

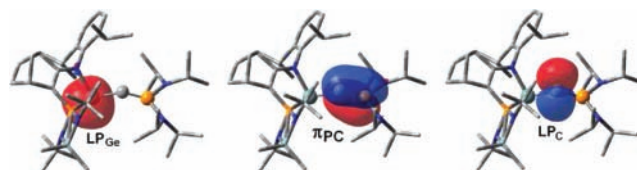


Figure 3. Most representative natural bond orbitals for **4a-III**.

the theoretically predicted values of 1.862–1.887 Å for germynes with electron-withdrawing and π -donating substituents (F or OH).^{9d} The trigonal-planar geometry around the P2 atom ($\Sigma\theta_{P2\alpha} = 359.7^\circ$), and the extremely short P2–C bond distance (1.549 Å) clearly indicate a strong π interaction between the phosphino substituent and the germyne fragment. Indeed, the P2–C bond length is in the range expected for phosphinocarbenes¹⁵ or phosphalkynes.¹⁷ Nevertheless, in spite of the P2–C multiple-bond character, the trigonal-planar phosphino fragment is strongly twisted relative to the P2–C–Ge fragment, with a N2–P2–C–Ge torsion angle of -73.7° . This value is even larger than that reported for methylenephosphonium salts [(iPr₂N)₂P=C(TMS)₂].¹⁸ These results clearly support the biscarbenoid structure of type **VI**, which is completely different from that of silicon analogue **A**, which shows a multiple-bonded structure of type **V**.

DFT calculations on **4a** and **4b** indicated that the structures **4a-I** presenting Ge–C triple bonds with a linear geometry around the germyne carbon atom, similar to the case of the silyne analogue,¹² are not energy minima on the respective potential energy surfaces (Figure 2). Instead, in the case of **4b**, we found a trans-bent structure (**4b-II**) as a local energy minimum, presenting a Ge–C double bond with a lone pair on the central carbon atom. However, the most stable isomer of **4b** is similar to the experimentally obtained structure with P–C double-bond character (**4a-III**). Isomer **4b-III** is more stable than **4b-II** by ca. 10 kcal/mol. In the case of **4a**, only isomer **4a-III** could be located and characterized as a true energy minimum. This difference might result from a distortion of the molecules for steric reasons. Indeed, **4a** with a more hindered phosphine ligand is more strongly twisted than **4b** (calculated N2–P2–C–Ge twist angles: 84.89° for **4a**, 26.28° for **4b**). However, in both compounds **4a** and **4b**, the Ge–C multiple-bonding character is not favored because of the partial stabilization of the germyne by the cyclic phosphines as well as strong π donation from the exocyclic bis(diisopropylamino)phosphine moiety, thus resulting in a stabilization of the C=P(NⁱPr)₂ unit. Indeed, natural bond orbital (NBO) analysis of **4a-III** showed the presence of a lone pair on the germanium atom (LP_{Ge}) and on the carbon atom (LP_C) as well as a P–C π bond (Figure 3). Interestingly, in contrast to LP_{Ge} having enhanced s character [$s(64.37\%)$, $p(35.54\%)$, $d(0.09\%)$], LP_C shows extremely high p character

Scheme 2. Isomerization of 4a and 4b

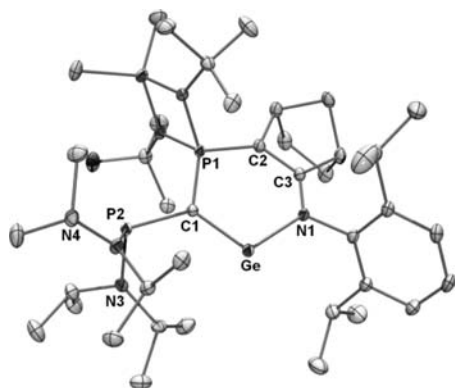
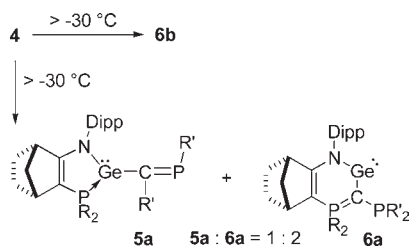


Figure 4. Molecular structure of **6a**. Thermal ellipsoids represent 30% probability. H atoms have been omitted for clarity. Selected bond lengths (Å) and angles (deg): Ge–C1, 1.9023(15); Ge–N1, 1.9149(13); C1–P1, 1.7192(15); C1–P2, 1.8382(15); P1–C2, 1.7489(16); C2–C3, 1.376(2); C3–N1, 1.356(2); N1–Ge–C1, 103.18(6); Ge–C1–P1, 122.36(8); C1–P1–C2, 108.97(7); P1–C2–C3, 128.25(12); C2–C3–N1, 128.06(14); C3–N1–Ge, 125.60(10); P1–C1–P2, 113.85(8); Ge–C1–P2, 123.17(8).

[s(1.88%), p(98.09%), d(0.04%)], indicating that the central carbon is sp-hybridized in spite of the bent structure of **4a** (calcd Ge–C1–P2 = 145.83°).

Like silynes **A**,¹² germynes **4** are thermally unstable and undergo an isomerization reaction above –30 °C. However, in contrast to **A**, which transforms selectively into a phosphalkene derivative via a 1,2-migration of a diisopropylamino group from phosphorus to the carbon center, the isomerization of **4a** affords a mixture of phosphalkene derivative **5a** and germylene **6a**. The formation of the second isomer **6a** involves the migration of the phosphine ligand from the germanium to the carbon center (Scheme 2). Germylene **6a** was systematically obtained as the major product (**5a**:**6a** = 1:2), in agreement with the DFT calculations, which indicated that the reactions are highly exothermic (ΔE_{5a-4a} = 25.22 kcal/mol, ΔE_{6a-4a} = 25.84 kcal/mol) and that **5a** and **6a** are very close in energy (ΔE_{6a-5a} = 0.6 kcal/mol). In contrast, the isomerization of **4b** leads to the exclusive formation of germylene **6b**, probably because of the presence of a less hindered phosphine ligand, which probably migrates more easily. Germylenes **6** are stable under inert conditions at room temperature and were fully characterized in solution as well as in the solid state in the case of **6a** (Figure 4).¹⁹ The most striking features of **6a** are the Ge–C1 (1.902 Å) and Ge–N1 (1.915 Å) bond lengths, which are slightly short for single bonds, indicating that the germylene center is well-stabilized by two π -donating groups such as amino and phosphonium

ylide. These structural properties are similar to those previously reported for a cyclic amino–enamino germylene.²⁰

In conclusion, we have successfully synthesized and fully characterized **4**, the first isolable germanium analogues of alkynes, which are stabilized by coordination of a phosphine ligand. In the case of **4a**, XRD analysis indicated a quite long Ge–C bond length for a triple bond and an extremely short P–C bond length. Germynes **4** rearrange at room temperature, affording a phosphalkene **5** (a typical reaction for singlet phosphinocarbenes) and a new stable N-heterocyclic germylene **6**.²¹ The results shown here demonstrate the significant differences not only in the structure of **4** but also in its chemical behavior with respect to the silicon analogue **A**. Further studies of the reactivity of this new species are under active investigation.

■ ASSOCIATED CONTENT

S Supporting Information. Experimental, computational, and crystallographic data, including CIF files. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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■ ACKNOWLEDGMENT

We are grateful to the CNRS, ANR (NOPROBLEM), MICINN (CSD2007-00006), and PCP (Nouveaux Ligands) for financial support.

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