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From a Phosphaketenyl-Functionalized Germylene to 1,3-Digerma-2,4-diphosphacyclobutadiene

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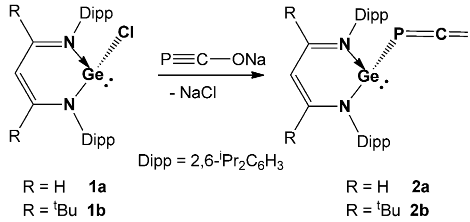
In memory of Malcolm Chisholm

Abstract: *The first 4π-electron resonance-stabilized 1,3-digerma-2,4-diphosphacyclobutadiene* $[L^H{}_2Ge_2P_2]$ **4** $(L^H = CH[CHNDipp]_2$ *Dipp* $= 2,6\text{-}^iPr_2C_6H_3)$ *with four-coordinate germanium supported by a β-diketiminate ligand and two-coordinate phosphorus atoms has been synthesized from the unprecedented phosphaketenyl-functionalized N-heterocyclic germylene* $[L^HGe\text{-}P{=}C{=}O]$ **2a** *prepared by salt-metathesis reaction of sodium phosphaethynolate* $(P{\equiv}C{-}ONa)$ *with the corresponding chlorogermylene* $[L^HGeCl]$ **1a**. *Under UV/Vis light irradiation at ambient temperature, release of CO from the P=C=O group of* **2a** *leads to the elusive germanium–phosphorus triply bonded species* $[L^HGe{\equiv}P]$ **3a**, *which dimerizes spontaneously to yield black crystals of* **4** *as isolable product in 67% yield. Notably, release of CO from the bulkier substituted* $[L^{tBu}Ge\text{-}P{=}C{=}O]$ **2b** $(L^{tBu} = CH[C(^tBu)N\text{-}Dipp]_2)$ *furnishes, under concomitant extrusion of the diimine* $[DippNC(^tBu)]_2$, *the bis-N,P-heterocyclic germylene* $[DippNC(^tBu)C(H)PGe]_2$ **5**.

Molecules bearing multiple bonds between two heavier main-group elements are often elusive intermediates. By taking advantage of kinetic and/or thermodynamic stabilization strategies, such highly reactive species can nevertheless be turned into classes of compounds that are isolable.[1] In this context, heteronuclear multiple bonds between the heavier Group 14 and 15 elements have attracted much attention owing to their unique reactivity and electronic properties.[1,2] After the successful synthesis of an isolable Si=P compound reported by Bickelhaupt and co-worker in 1984,[3] several striking examples featuring multiply bonded heavier Group 14 and 15 elements have been isolated and structurally characterized.[1–5] However, the synthesis of more unsaturated triply bonded RE≡P (E = Si, Ge) species remains challenging because of the even higher tendency of E≡P bonds to undergo dimerization or oligomerization.

Recently, when we attempted to synthesize a stable Si−P triply bonded compound, a phosphasilyne [LSi≡P], we could only isolate its corresponding head-to-tail dimer, the 4π-electron resonance-stabilized 2,4-disila-1,3-diphosphacyclobutadiene.[4k] Herein, we wish to report the unexpectedly facile access to the first head-to-tail dimer of a phosphagermyne, starting from a novel phosphaketenyl-functionalized germylene. Furthermore, an unprecedented N,P-heterocyclic bis-germylene could be synthesized via a remarkable and unexpected condensation reaction.

At first, the *N*-heterocyclic chlorogermylenes $[L^HGeCl]$ **1a** $(L^H = CH[CHNDipp]_2$, $Dipp = 2,6\text{-}^iPr_2C_6H_3)$ and $[L^{tBu}GeCl]$ **1b** $(L^{tBu} = CH[C(^tBu)NDipp]_2)$[6] were allowed to react with one molar equivalent of sodium phosphaethynolate, a convenient anionic phosphorus atom transfer reagent for which a synthesis was recently developed,[7] to give the phosphaketenyl germylenes **2a** and **2b**, respectively, in quantitative yield according to ^1H and ^{31}P NMR spectroscopy (Scheme 1). Both were isolated as yellow crystals in 90 and 92% yields, respectively. Their constitutions and compositions were proved by ^1H, ^{13}C, ^{31}P NMR spectroscopy, elemental analyses and high resolution-mass spectrometry (HR-MS) (see the Supporting Information).



Scheme 1. Synthesis of the phosphaketenyl-substituted germylenes **2a** and **2b** from the corresponding chlorogermylenes **1a** and **1b**, respectively.

The ^{31}P NMR spectrum of **2a** and **2b** shows a singlet at $\delta = -298.9$ and -304.9 ppm, respectively. Both resonances are shifted to higher frequencies compared to $Ph_3Ge\text{-}P{=}C{=}O$ $(\delta = -344.0$ ppm$)$.[8] The IR spectra of **2a** and **2b** exhibit intense stretching vibrations at $\tilde{\nu} = 1895$ and $1887\ cm^{-1}$, respectively, for the PCO groups $(Ph_3Ge{-}P{=}C{=}O$: $\tilde{\nu} = 1954\ cm^{-1})$.[8] No evidence for the presence of the corresponding phosphaethynolato germylene isomer $(LGe{-}O{-}C{\equiv}P)$ could be observed both in the solid state (IR spectroscopy)

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and in solution (^{1}H, ^{31}P NMR spectroscopy). In line with that, the latter hypothetical isomers are thermodynamically less stable than the phosphaketenyl derivatives by about 10 kcal mol^{-1} according to calculations (see the Supporting Information).

The molecular structures of **2a** and **2b** were established by single-crystal X-ray diffraction studies. Compound **2a** crystallizes in the monoclinic space group $P2_1/c$ with two independent molecules in the asymmetric unit (only one is shown in Figure 1, left). The germanium centers of both independent molecules adopt a trigonal pyramidal geometry reminiscent of the previously reported β-diketiminato Ge^{II} complexes,[6] implying that the vertexes of the Ge atoms are occupied by a lone pair of electrons. The presence of almost linear PCO moieties (178.0(2) and 177.8(2)°), coordinated to the Ge atom via the phosphorus atom, is consistent with the respective IR and NMR spectroscopic data. The Ge−P distances of 2.4762(5) and 2.4775(5) Å are significantly longer than that calculated for Ge-P single bond in Ph_3Ge−P=C=O (2.398 Å, at the B3LYP/cc-pVDZ(-PP) level).[8] In contrast, the P−C distances of 1.643(2) and 1.639(2) Å are shorter than the calculated values for Ph_3Ge-P=C=O (1.684 Å), while the C−O bond distances (1.166(3) and 1.170(3) Å) are comparable to that of Ph_3Ge-P=C=O (1.165 Å).

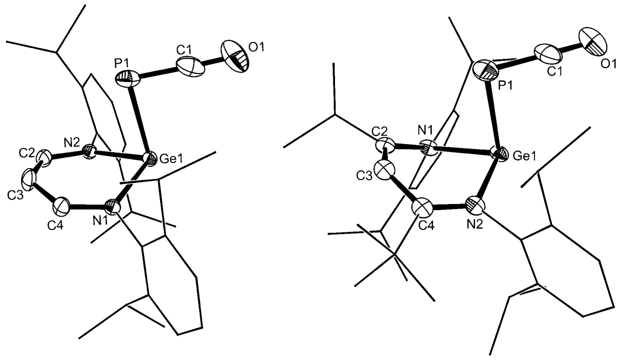
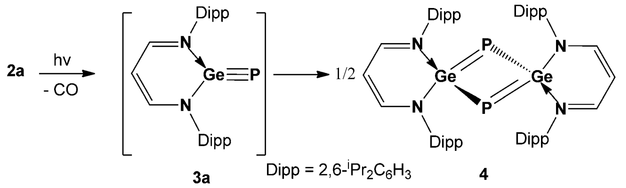


Figure 1. Molecular structures of **2a** (left) and **2b** (right).[11] Ellipsoids are set at 50% probability; H atoms are omitted for clarity. Selected interatomic distances [Å] and angles [°] for **2a**: Molecule 1: Ge1–N2 1.997(1), Ge1–N1 2.001(1), Ge1–P1 2.4762(5), P1–C1 1.643(2), O1–C1 1.166(3); N2-Ge1-N1 89.89(5), O1-C1-P1 178.0(2); Molecule 2: Ge1–N1 1.993(1), Ge1–N2 2.008(1), Ge1–P1 2.4775(5), P1–C1 1.639(2), O1–C1 1.170(3); N1-Ge1-N2 89.80(5), O1-C1-P1 177.8(2). For **2b**: Ge1–N1 1.971(2), Ge1–N2 2.016(2), Ge1–P1 2.5010(8), P1–C1 1.625(4), O1–C1 1.174(5), N1–C2 1.352(3), N2–C4 1.329(3), C2–C3 1.394(4), C3–C4 1.420(4); N1-Ge1-N2 93.09(8), O1-C1-P1 178.7(4).

Compound **2b** crystallizes in the triclinic space group $P\bar{1}$ (Figure 1, right). Although the geometry of the molecular structure resembles **2a**, the six-membered C_3N_2Ge ring of **2b** is more severely puckered than that of **2a** and the Ge−P distance is slightly longer (2.5010(8) Å vs. 2.4762(5) and 2.4775(5) Å in **2a**). The latter geometric difference can be rationalized by more steric congestion for **2b** caused by the two *tert*-butyl groups on the β-diketiminate backbone compared to **2a**.

Both **2a** and **2b** are stable in solution and in the solid state as long as air and moisture are excluded. They even survive in benzene heated to 80 °C in sealed NMR tubes. As their UV/Vis spectra exhibit absorption maxima at 325 and 320 nm, respectively, owing to the π–π* transitions of the P=C bonds (see the Supporting Information), respectively, irradiation with UV/Vis light may result in the cleavage of CO from the PCO groups.[9] In fact, irradiation of toluene solutions of **2a** in the UV/Vis region of $\lambda = 320$–400 nm for one hour at room temperature causes darkening of the yellow solutions and evolution of CO. After completion of the liberation of CO, the ^{31}P NMR spectrum of the resulting solution shows only one new singlet at $\delta = 87.0$ ppm, which is strongly shifted to higher frequency compared to its precursor **2a** ($\delta = -298.9$ ppm). Upon standing at room temperature for two days, black crystals of $[L^H{}_2Ge_2P_2]$ **4** are obtained in 67% yield in the reaction solution (Scheme 2). The ^{31}P chemical shift of solid **4** obtained from CP-MAS ^{31}P NMR measurement is almost identical with the value observed in solutions ($\delta = 88$ vs. 87 ppm).



Scheme 2. Formation of the phosphagermyne **3a** as presumed intermediate and its head-to-tail dimerization to give the 1,3-digerma-2,4-diphosphacyclobutadiene **4**.

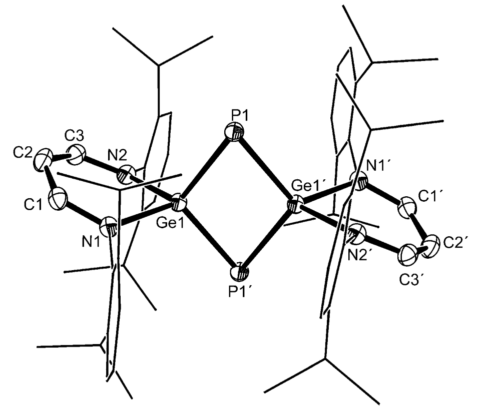
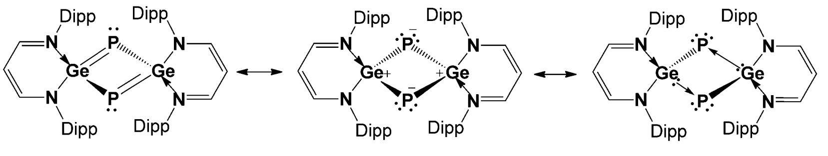


Figure 2. Molecular structure of **4**.[11] Ellipsoids are set at 50% probability; H atoms are omitted for clarity. Symmetry transformations used to generate equivalent atoms with (′): $-x+1,-y,-z+1$. Selected interatomic distances [Å] and angles [°]: Molecule 1: Ge1–N1 1.985(2), Ge1–N2 1.988(2), Ge1-P1′ 2.2658(5), Ge1–P1 2.2717(5), Ge1–Ge1′ 2.7443(4), P1–Ge1′ 2.2658(5); N1-Ge1-N2′ 88.83(7), P1′-Ge1-P1 105.57(2), Ge1′-P1-Ge1 74.43(2); Molecule 2: Ge1–N1 1.983(2), Ge1–N2 1.988(2), Ge1–P1 2.2550(6), Ge1–P1′ 2.2673(6), Ge1–Ge1′ 2.7401(4), P1–Ge1′ 2.2673(6); N1-Ge1-N2 89.32(7), P1-Ge1-P1′ 105.41(2), Ge1-P1-Ge1′ 74.59(2).

Compound **4** crystallizes in the monoclinic space group $P2_1/c$ with two independent molecules in the asymmetric unit (only one is shown in Figure 2). The single-crystal X-ray diffraction study reveals a dimer structure with a planar four-membered Ge_2P_2 ring perpendicular to both slightly puckered six-membered C_3N_2Ge cycles. Thus both Ge atoms achieve a distorted tetrahedral geometry and form a diamond-shaped Ge_2P_2 moiety. The Ge–P distances, ranging from 2.2550(6) to 2.2717(5) Å, are significantly shorter than those observed in **2a** (2.4762(5) and 2.4775(5) Å), but longer than the Ge=P bonds in reported phosphagermenes (2.138(3)–2.175(1) Å).[5] Such intermediate values of the Ge–P distances in **4** indicate already partial double bond character, while the similarity of these Ge–P bonds in the Ge_2P_2 cycle suggests extensive σ- and π-electron resonance stabilization within the Ge_2P_2 ring (see below for confirmation by DFT calculations). It is noteworthy that the Ge⋯Ge interactions in the two independent molecules amount to 2.7401(4) and 2.7443(4) Å while the P⋯P separations are 3.598 and 3.614 Å, respectively. Thus the Ge_2P_2 rings feature very acute Ge-P-Ge angles (74.43(2) and 74.59(2)°) vs. obtuse P-Ge-P angles (105.57(2) and 105.41(2)°).

To establish the electronic structure of **4**, we carried out DFT calculations at the B3LYP/6-31G(d)[Ge, P: cc-pVTZ(-PP)] level using initial geometric parameters observed by X-ray diffraction analysis. The optimized structure closely resembles the experimental data (see the Supporting Information). The WBI of the Ge–P bonds are somewhat larger than unity, which may indicate some double-bond character (Supporting Information, Table S6). However, natural bond orbital (NBO) analysis results in a Ge–P single bond and two lone pairs of electrons at each P center, and the NPA charges are also relatively high on the P atoms (−0.71). The repulsion of the negative charge at the ylidic P centers is responsible for the observed rhombus-like distortion of the Ge_2P_2 cycle in **4**. Similar structure deviation from a perfect square of a tetrasilabutadiene was recently described by Tamao et al.[10] Accordingly, the relatively short Ge⋯Ge distance of ca. 2.74 Å does not imply a bonding interaction between the two germanium centers consistent with the calculated WBI of 0.01 (Supporting Information). The degree of delocalization of σ- and π-electrons of the Ge_2P_2 ring has also been investigated. The nucleus-independent chemical shift (NICS) values are slightly negative (NICS(0): −5.9 ppm, NICS(1): −2.4 ppm), suggesting little or no aromaticity, but definitely not antiaromaticity as the resonance form **4A** could imply (Scheme 3). The electronic situation is best described by the ylide-like resonance structure **4B**, while the germylene phosphinidene structure **4C** seems much less relevant.

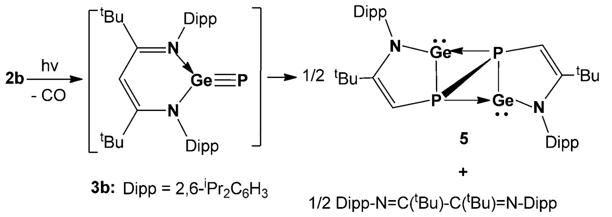


4A **4B** **4C**

Scheme 3. Resonance structures of **4**.

Compound **4** is the first example of a 4π-electron resonance-stabilized 1,3-digerma-2,4-diphosphacyclobutadiene derivative. Although the mechanism to **4** is still unknown, we propose that the CO release from **2a** under irradiation led to the desired product [L^{H}Ge≡P] **3a** initially which dimerizes in a head-to-tail fashion to yield **4** as sole product (Scheme 2). This is confirmed by calculations which reveal that the dimer species **4** is more stable than the two **3a** molecules by 68.2 kcal mol^{-1} and the dimerization barrier is very small (3.1 kcal mol^{-1}). As expected, the electronic structure of **3a** established by DFT calculations reveals a polar Ge≡P bond with a WBI of 2.46. Furthermore, three bonds between the Ge and P atoms are suggested by the NBO analysis and a very short Ge–P distance (2.061 Å) is found in the optimized structure.

Interestingly, in the case of **2b**, the situation changes drastically owing to the large steric congestion caused by the two ^{t}Bu groups at the backbone of the β-diketiminate ligand. DFT calculations predict that the dimerization of the [L^{tBu}Ge≡P] species **3b** (Scheme 4) to give its hypothetical head-to-tail dimer requires a much higher activation energy of 12.2 kcal mol^{-1} because of the steric hindrance. Moreover, the resulting [$L^{tBu}{}_2Ge_2P_2$] dimer is much less stable (−23.2 kcal mol^{-1}) than **4** (−68.2 kcal mol^{-1}) with respect to the corresponding Ge≡P monomers. This is in agreement with the experimental result obtained from the irradiation of **2b** under the same reaction conditions. The latter gives rise to the novel N,P-heterocyclic bis-germylene **5**, [DippNC(^{t}Bu)C(H)PGe]$_2$, and the diimine, [Dipp-NC(^{t}Bu)]$_2$, as sole products according to ^{1}H and ^{31}P NMR spectroscopy, high-resolution ESI mass spectrometry, and single-crystal X-ray diffraction analysis (Scheme 4). The results by DFT calculations confirm that the generation of **5**, under elimination of the diimine [Dipp-NC(^{t}Bu)]$_2$, has a lower activation barrier (9.8 kcal mol^{-1}) and a larger energy gain (−71.4 kcal mol^{-1}) than the formation of the hypothetical [$L^{tBu}{}_2Ge_2P_2$] dimer product (see Figure S9 in Supporting Information).



Scheme 4. Formation of the phosphagermyne **3b** as transient species and its conversion to the *N*,*P*-heterocyclic bis-germylene **5** under liberation of the diimine [Dipp-NC(^{t}Bu)]$_2$.

The molecular structure of **5** determined by an X-ray diffraction analysis reveals a dimeric structure also featuring a planar four-membered Ge_2P_2 ring (Figure 3). However, the P–P distance of 2.388(1) Å indicates a single bond. Additionally, the two Ge atoms are coordinated each by the two P

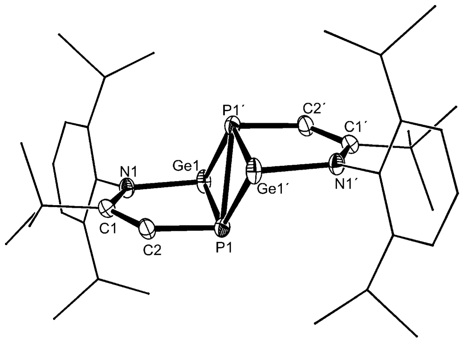


Figure 3. Molecular structure of **5**.[11] Ellipsoids are set at 50% probability; H atoms are omitted for clarity. Symmetry transformations used to generate equivalent atoms with (′): $-x+2,-y+2,-z+2$. Selected interatomic distances [Å] and angles [°]: Ge1–N1 1.917(2), Ge1–P1 2.3888(6), Ge1–P1′ 2.4848(6), P1–C2 1.785(2), P1–P1′ 2.388(1), P1–Ge1′ 2.4848(6), N1–C1 1.395(3), C1–C2 1.366(3); N1-Ge1-P1 86.47(5), N1-Ge1-P1′ 97.06(5) P1-Ge1-P1′ 58.64(2), C2-P1-Ge1 92.43(7), C2-P1-Ge1′ 94.06(7), Ge1-P1-Ge1′ 121.36(2).

atoms and an N atom of the cleaved β-diketiminate ligand, adopting a trigonal-pyramidal geometry typical for a donor-supported three-coordinate Ge$^{\text{II}}$ center. The Ge⋯Ge separation of 4.250 Å excludes any bonding interaction between the Ge atoms. The Ge−P distances (Ge1−P1 2.3888(6) Å and Ge1−P1′ 2.4848(6) Å) differ only slightly, implying electron delocalization over the Ge$_2$P$_2$ cycle. The latter bonds are significantly longer than the Ge−P bonds in **4** (2.2550(6)–2.2717(5) Å), which is most likely due to different valence of the germanium atoms in the two compounds (see the Supporting Information).

In summary, we reported the facile synthesis and structural characterization of the first 4π-electron resonance-stabilized 1,3-digerma-2,4-diphosphacyclobutadiene derivative [L$^{\text{H}}_2$Ge$_2$P$_2$] **4**, resulting from the phosphaketenyl-functionalized germylene [L$^{\text{H}}$Ge(PCO)] **2a** through release of CO and via the initial formation of the elusive phosphagermyne [L$^{\text{H}}$Ge$\equiv$P] **3a**. Unexpectedly, employing [L$^{\text{tBu}}$Ge(PCO)] **2b** with a bulkier ligand backbone, furnishes, after elimination of CO und [(Dipp-NC($^{\text{t}}$Bu))$_2$], the novel N,P-heterocyclic bis-germylene [(DippNC($^{\text{t}}$Bu)C(H)PGe)$_2$] **5** again via the corresponding [L$^{\text{tBu}}$Ge$\equiv$P] **3b** as presumed intermediate. Further investigations are devoted to the synthesis of isolable E$\equiv$P compounds (E = Si, Ge) by using modified more bulky substituted N-heterocyclic backbone ligands attached to the divalent Si$^{\text{II}}$ and Ge$^{\text{II}}$ atoms in suitable phosphaketenyl precursors.

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Keywords: germylenes · main-group chemistry · multiple bonds · phosphagermyne · β-diketiminates

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