

Striking reactivity of ylide-like germylene toward terminal alkynes: [4 + 2] cycloaddition *versus* C–H bond activation†

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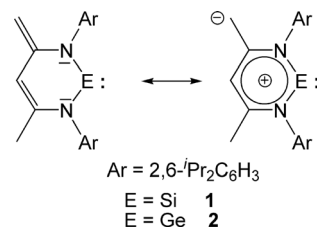
The isolable ylide-like *N*-heterocyclic germylene LGe: (**2**) {L = CH[(C=CH₂)CMe][N(aryl)]₂, aryl = 2,6-*i*-Pr₂C₆H₃} shows an unprecedented dual reactivity toward terminal alkynes: its reaction with acetylene leads *via* [4 + 2] cycloaddition to the novel intramolecular donor stabilised germylene **3**, while conversion of phenylacetylene furnishes the analogous cycloadduct **4** along with a C–H bond activation product, the novel *N*-donor stabilised alkynyl germylene **5**.

In recent decades, silylenes and germylenes have been the focus of considerable research due to their carbene-like properties.^{1–3} They are highly reactive and represent indispensable building blocks for the synthesis of unique low-coordinated silicon or germanium compounds with remarkable electronic features. Since the seminal work by Lappert and co-workers on isolable divalent Ge, Sn, and Pb carbene-like compounds,^{3a} even the isolation of silylenes and new types of germylenes stable at room temperature has been achieved by judicious choice of sterically demanding substituents on the Si(II) and Ge(II) atoms, which provide a kinetic and thermodynamic stabilisation with π -donor groups bonded to the divalent silicon or germanium atom. Taking advantage of the intramolecular stabilisation of low-valent silicon and germanium, respectively, by *N*-donor substitution, a number of isolable *N*-heterocyclic divalent germanium and silicon complexes have been synthesised.^{3–5a–c} Very recently, we developed a facile route to a novel type of donor-supported zwitterionic NHC-homologues,^{5d} the *N*-heterocyclic silylene LSi: **1**^{5a} and its germanium homologue LGe: (**2**) (Scheme 1).⁶

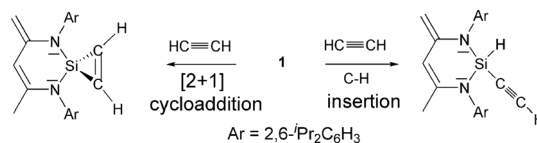
Owing to their unique ylide-like character, silylene **1** and germylene **2** show remarkably distinct reactivities toward both electrophiles and nucleophiles in comparison to the behaviour of other *N*-heterocyclic silylenes and germylenes, respectively.^{5–8} Interestingly, the 1,4-dipolar nature of **1** facilitates a marked preference for C–H insertion *versus* autocatalytic [2 + 1] cycloaddition of the C $\equiv$ C bond of terminal alkynes at divalent silicon (Scheme 2).⁸ Herein, we wish to report the remarkably different reactivity of germylene **2** toward terminal alkynes, affording the [4 + 2] cycloaddition products **3** and **4** as well as the 1,4-insertion (C–H bond activation) product **5**, respectively.

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† Electronic supplementary information (ESI) available: Synthesis, characterisation and crystallographic data of **3**, **4**, and **5**, and DFT calculations of model systems. CCDC reference numbers 695015–695017. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/b811952j



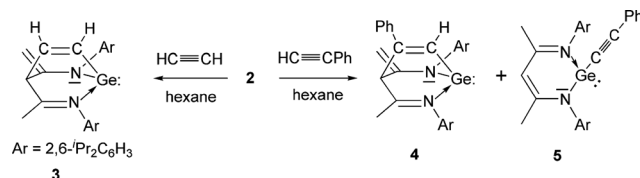
Scheme 1 The mesomeric forms of zwitterionic **1** and **2**.



Scheme 2 The dichotomic reactivity of **1** toward HC $\equiv$ CH.

Exposure of a brown-red solution of **2** in hexane to HC $\equiv$ CH at room temperature leads to a yellow solution, from which yellow crystals of the air-sensitive cycloadduct **3** can be isolated in 81% yield (Scheme 3). The composition and constitution of compound **3** are proven by elemental analysis, ¹H and ¹³C NMR spectroscopy (see ESI†). Solid **3** melts at 155 °C and undergoes slow decomposition without cycloreversion. Its structure has been established by single-crystal X-ray diffraction analysis (Fig. 1).

Compound **3** represents a new type of intramolecular donor stabilised *N*-heterocyclic germylene. The structural analysis revealed that **3** consists of a bicyclo[2,2,2]octane-like core with a C₅N₂Ge skeleton and Ge(II) and the γ -C atom as bridgehead atoms (Fig. 1). Thus the entire β -diketiminate ligand has undergone modification and the Ge and the γ -C atom are now in a non-planar GeN₂C₃ six-membered ring. Accordingly, the Ge(II) centre adopts a pyramidal coordination with the sum of bond angles of 267.4°, similar to the situation in related Ge(II) β -diketiminate complexes.^{3,4} The Ge1–N2 distance of 206.1(3) pm in **3** is significantly longer than that of the Ge1–N1 bond [198.5(3) pm], implying a stronger donor character for N2. The latter is consistent with pronounced shortening of the N2–C4 distance [130.6(4) pm] compared to that of the N1–C2 bond [135.1(4) pm]. The C30–C31 distance of the 1,2-ethylene-diyl bridge [132.1(5) pm] is in the common range of localised C=C distances. Moreover, the ¹H NMR spectrum of **3** reveals



Scheme 3 The reaction of **2** with HC $\equiv$ CH and HC $\equiv$ CPh.

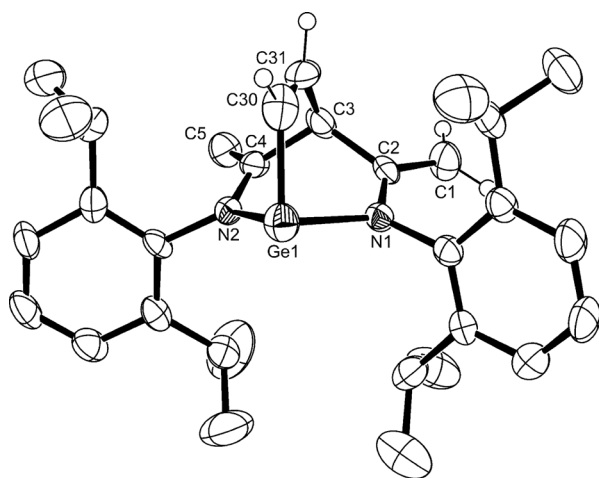


Fig. 1 The molecular structure of **3**. Thermal ellipsoids are drawn at 50% probability level. Hydrogen atoms, except those at C1, C30, and C31, are omitted for clarity. Selected bond lengths (pm) and angles ($^{\circ}$): Ge1–N1 198.5(3), Ge1–C30 199.1(4), Ge1–N2 206.1(3), N1–C2 135.1(4), C1–C2 137.3(4), N2–C4 130.6(4), C2–C3 151.1(5), C3–C4 151.3(5), C3–C31 157.8(5), C30–C31 132.1(5), N1–Ge1–C30 90.0(1), N1–Ge1–N2 89.7(1), C30–Ge1–N2 87.7(1), C2–C3–C4 113.6(3), C2–C3–C31 108.3(3), C4–C3–C31 107.4(3). The sum of angles at Ge 267.4.

a doublet of doublets ($^3J_{\text{HH}} = 6.7$ Hz, $^4J_{\text{HH}} = 1.3$ Hz) at 4.25 ppm for the γ -H atom in accordance with the aliphatic character of the γ -C bridgehead atom. In contrast, two doublets of doublets at much lower field [6.96 ($^3J_{\text{HH}} = 10.1$ Hz, $^3J_{\text{HH}} = 6.7$ Hz) and 7.60 ppm ($^3J_{\text{HH}} = 10.1$ Hz, $^4J_{\text{HH}} = 1.3$ Hz)] have been observed for the ^1H nuclei of the 1,2-ethylenediyl group. Similar low-field shifts of the hydrogen atoms in Ge-vinyl compounds have been previously observed for $\text{Me}_3\text{GeCH}=\text{CH}_2$.⁹

Interestingly, conversion of **2** with phenylacetylene in *n*-hexane leads to the analogous [2 + 4] cycloadduct **4** along with the alkynyl germylene **5** (Scheme 3). The products can be separated by fractional crystallisation and isolated in the form of yellow crystals in 67% (**4**) and 16% yield (**5**), respectively. They have been characterised by elemental analysis, mass spectrometry, ^1H and ^{13}C NMR spectroscopy (see ESI†). The ^1H NMR spectrum of **5** shows the presence of two chemically equivalent exocyclic β -methyl groups. In other words, the former exocyclic methylene group in **2** has been converted to a β -methyl group through 1,4-addition of the phenylacetylene (C–H bond activation) to the germylene. This and the molecular structure of **4** has been confirmed by X-ray diffraction analysis (Fig. 2 and 3). As expected, the characteristic metric features of **4** are similar to those of **3** despite the terminal phenyl group bonded to one of the C atoms of the 1,2-ethylenediyl bridge. Apparently, the cycloaddition of phenylacetylene occurs regioselectively owing to steric hindrance induced by the large aryl groups at nitrogen. In line with that, germylene **2** does not react with diphenylacetylene even at elevated temperatures. Compound **5** is the second example of an isolable alkynyl germylene characterised structurally.¹⁰ It possesses a pyramidally coordinated Ge(II) atom and reveals an almost planar GeN_2C_3 ring similar to the situation in related β -diketiminato complexes of divalent germanium.^{3,4} The $\text{C16}\equiv\text{C17}$ distance of 121.9(5) pm in **5** is in the typical range for $\text{C}\equiv\text{C}$ distances in other alkyne derivatives and

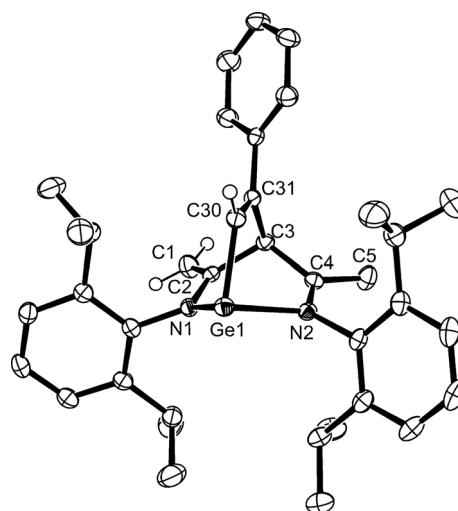


Fig. 2 The molecular structure of **4**. Thermal ellipsoids are drawn at 50% probability level. Hydrogen atoms, except those at C1 and C30, are omitted for clarity. Selected bond lengths (pm) and angles ($^{\circ}$): Ge1–N1 195.9(1), Ge1–C30 201.6(2), Ge1–N2 210.0(1), N1–C2 137.8(2), C1–C2 134.4(2), N2–C4 129.0(2), C2–C3 152.4(2), C3–C4 151.8(2), C3–C31 154.6(2), C30–C31 132.6(2), C31–C32 148.7(2), N1–Ge1–C30 91.05(6), N1–Ge1–N2 89.09(5), C30–Ge1–N2 84.82(6), C4–C3–C2 113.6(1), C4–C3–C31 107.9(1), C2–C3–C31 109.2(1). The sum of angles at Ge 265.0.

identical to the respective value observed in $\text{Mamx-Ge}(\text{C}\equiv\text{CPh})$ ($\text{Mamx} = \text{methylamino-methyl-}m\text{-xylyl}$).¹⁰

The question arises, how are these compounds formed in the reaction of **2** with alkynes? Although the mechanism is still unknown, we reasoned that the [4 + 2] cycloaddition is promoted by the electrophilic character of the two-coordinate germanium(II) centre and the nucleophilic character of the endocyclic γ -C atom in the GeN_2C_3 ring in **2**. Related cycloaddition reactions of unsaturated organic substrates to β -diketiminato ligands have been previously observed for transition metal β -diketiminato cations [e.g. Ru(II) ¹¹ and Fe(II) ¹²] and for a Al(III) β -diketiminato cation,¹³ respectively. The reactivity of **2** toward alkynes is in marked contrast to that of the silylene homologue **1** which leads exclusively to Si(IV) addition products {[2 + 1] cycloaddition of $\text{C}\equiv\text{C}$ and Si(II) vs. 1,1-insertion of the C–H bond at Si(II) }.⁸ This can be explained by the pronounced inert-electron pair effect of Ge(II) vs. Si(II) and the lower basicity of the lone-pair electrons at Ge(II) , respectively. In fact, the formation of **3** and **4** is supported by density functional theory (DFT) calculations using the model system **2A**, in which the 2,6-*i*-Pr₂C₆H₃ groups at nitrogen have been replaced by phenyl (see ESI†). The calculations revealed that, in contrast to the reactivity of the silicon-homologue **2A**, the [4 + 2] cycloaddition product **3A** is the thermodynamic product (-126.4 kJ mol⁻¹) with a remarkably low barrier of only 33.5 kJ mol⁻¹ for the reaction of **2A** with $\text{HC}\equiv\text{CH}$ (Scheme 4). Interestingly, C–H bond activation of $\text{HC}\equiv\text{CH}$ with **2A** leads to the second stable product of the system (-98.7 kJ mol⁻¹), the 1,4 adduct **5A**, with a higher activation energy of 87.7 kJ mol⁻¹. The latter barrier is relatively high and explains the absence of such a species in the case of the reaction of **2** with $\text{HC}\equiv\text{CH}$. Apparently, the situation is drastically changed by applying $\text{PhC}\equiv\text{CH}$ which possesses a more acidic C–H bond and leads

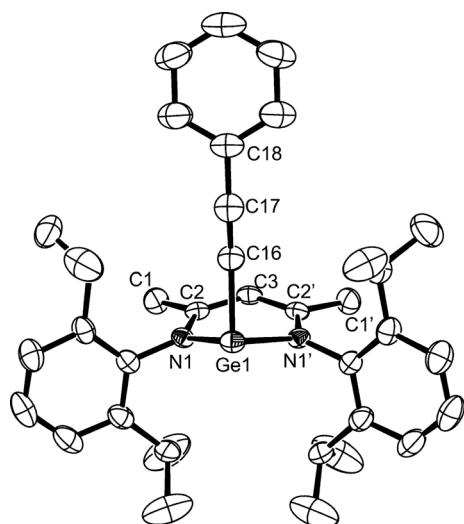
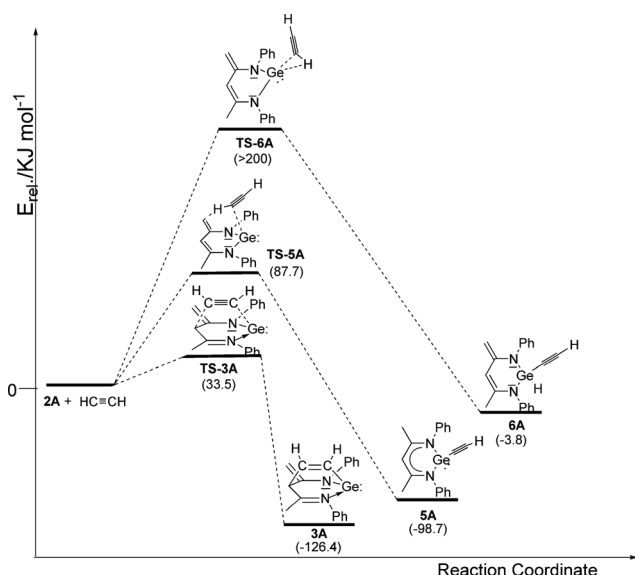


Fig. 3 Molecular structure of **5**. Thermal ellipsoids are drawn at 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (pm) and angles ($^{\circ}$): Ge1–C16 197.6(4), Ge1–N1 198.5(2), N1–C2 134.5(3), C2–C3 139.0(3), C16–C17 121.9(5), C16–Ge1–N1 93.35(9), N1'–Ge1–N1 91.3(1), C2–C3–C2' 127.9(3), C17–C16–Ge1 171.0(3), C16–C17–C18 176.6(4). The sum of angles at Ge is 278. Symmetry transformations used to generate equivalent atoms ($'$): $x, -y + 3/2, z$.

to the corresponding compound **5** at least as a minor product. As in the silicon-homologue of **2A**, formation of the 1,1-adduct **6A** by direct insertion of Ge(II) into the C–H bond faces a very high activation barrier (>200 kJ mol $^{-1}$). In contrast to the silicon case, **6A** is thermodynamically disfavoured compared to its tautomer **5A** (Scheme 4).

Striking differences in comparison with the Si(II) homologue result also for the [2+1] cycloaddition product of **2A** with HC $\equiv$ CH, that is, the corresponding germacyclop-3-ene, which is thermodynamically disfavoured by 53.5 kJ mol $^{-1}$. In contrast, the silicon-homologues react readily to the corresponding *N*-heterocyclic silacyclop-3-enes which result as a kinetic



Scheme 4 An energy profile for the reaction of **2A** with HC $\equiv$ CH, including DFT-calculated structures of the model compounds **3A**, **5A**, **6A** and their corresponding transition states **TS-3A**, **TS-5A** and **TS-6A**, respectively.

product in an autocatalytic process and can be isolated in high yields (Scheme 2).⁸ It should be mentioned here that isolable germacyclop-2-enes have been generated employing transient germynes and acetylene.¹⁴

In summary, the unprecedented reactivity of the ylide-like germylene **2** toward terminal alkynes is reported. Reaction of the zwitterionic germylene **2** with HC $\equiv$ CR leads to the unexpected [4+2] cycloadducts **3** (R = H) and **4** (R = Ph) but also to the second isolated alkynyl germylene **5** (R = Ph). The novel compounds represent remarkably strong nucleophilic Ge(II) ligands in metal coordination chemistry for catalysis. Respective investigations are currently underway.

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