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- [11] Comparisons between ¹H and ¹³C NMR spectra of **L** and **LOH** allowed us to unambiguously attribute the inserted oxygen position. In fact, the signal at δ = 6.63 corresponding to the *o*-H for **L** is replaced by two signals at δ = 6.63 and 6.42 in a 2:1 ratio for **LOH**. A similar trend is observed in the ¹³C NMR spectrum (for the *o*-C of the phenyl ring signals appear at δ = 108.5 and 105.5 for **LOH**, but only at δ = 105.0 for **L**). ESI-MS for **LOH** (CH₂Cl₂; positive-ion mode): *m/z*: 619 (100%) for [LOH + H⁺].
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- [16] Accordingly, the pendant product of the N-dealkylation of the ligand, 3,4,5-trimethoxybenzaldehyde, has been quantitatively detected.
- [17] Experimental conditions: complex/alkane/H₂O₂ 1/1100/10 in acetonitrile inside a glove box (dioxxygen content less than 1 ppm) using syringe pump conditions; delivering time = 30 min [complex] = 0.7 mM.
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A Route to a Germanium–Carbon Triple Bond: First Chemical Evidence for a Germyne**

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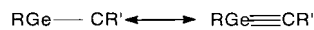
Since the isolation of the first disilene, a compound containing a silicon–silicon double bond, in 1981,^[1] many stable compounds with a double bond involving the Group 14 elements Si, Ge, and Sn have been synthesized.^[2] In contrast, compounds containing a triple bond to a Group 14 element other than C remained unknown. Power^[3] described recently a lead analogue of an alkyne (ArPbPbAr) but more consistent with a diplumbylene form. However, some compounds with triple bonds to Si were identified by spectroscopy or by

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various other methods.^[4] Germaioscyanides $\text{:Ge}\equiv\text{NR}$ have only been detected by photoelectron spectroscopy,^[5] whereas in coordination chemistry, stable transition metal germylyne complexes have been reported and structurally characterized since 1996.^[6] No triple bond to tin has yet been described.

Besides the difficulty in isolating such a triply bonded compound and the possibility that more stable isomers exist, the major obstacle remains to find a suitable synthetic method. We considered a potential route to germynes $\text{RGe}\equiv\text{CR}'$ from a germylene–carbene structure (Scheme 1).

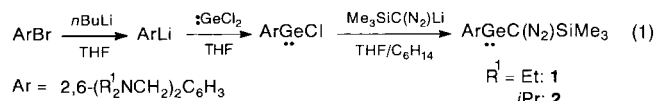


Scheme 1. Resonance forms: germylene–carbene and germyne.

Coupling reactions between germylenes (or stannylenes) and carbenes that provide convenient access to $\text{Ge}-\text{C}$ and $\text{Sn}-\text{C}$ double bonds^[7,8] prompted us to extend such a methodology to the formation of a germanium–carbon triple bond from a σ -bonded germylene–carbene compound. Generation of a carbene moiety adjacent to a Group 14 element bearing both a lone pair and a vacant p orbital^[9] appears to be an attractive method for the synthesis of a triply bonded metal–carbon species. Diazogermynes $\text{RGeC}(\text{N}_2)\text{R}'$ may be convenient precursors for the formation of such a unit by photolysis or thermolysis. We describe here the synthesis and the structure of diazogermynes $\text{ArGeC}(\text{N}_2)\text{SiMe}_3$ and an initial study of their photochemical behavior.

The 2,6-bis[(dialkylamino)methyl]phenyl groups $(\text{R}_2\text{NCH}_2)_2\text{-C}_6\text{H}_3$ (Ar) are suitable ligands because of their steric bulk and, in particular, their stabilizing effect due to intramolecular coordination of the nitrogen lone pair to empty orbitals on the metal atom. The use of this kind of ligand has allowed the preparation of sensitive derivatives of main group elements, such as gallium and indium halides ($\text{R}^1 = \text{Me}, \text{Et}$)^[10a-c] as well as a chlorostannylene ($\text{R}^1 = \text{Me}$).^[10d]

The diazogermynes were obtained in good yields by one-pot synthesis [Eq. (1)]. Compounds **1** and **2** are readily soluble



in hydrocarbon and ether solvents and have been fully characterized. Whereas **1** is a yellow, viscous oil, **2** is crystalline, and single crystals suitable for an X-ray structure determination were grown from pentane at -20°C . The structure analysis^[11] showed **2** to be monomeric in the solid state (Figure 1).

The Ar ligand is bound to germanium in a bidentate fashion with a σ bond to the *ipso*-carbon atom C5 and intramolecular coordination of the N atom of a CH_2NiPr_2 side chain. The $\text{Ge1}-\text{N3}$ distance of 2.35(9) Å is, as expected, longer than the a normal $\text{Ge}-\text{N}$ σ bond (1.92 Å^[12a]) but much shorter than the sum of the van der Waals radii (3.74 Å^[12b]). The $\text{Ge}-\text{N4}$ distance (3.05(3) Å) indicates a weak interaction between the N atom of the other side chain and the metal atom. The coordination sphere of germanium is completed by the $\text{Ge1}-\text{C1}$ bond, which is oriented almost orthogonal (96.8°)

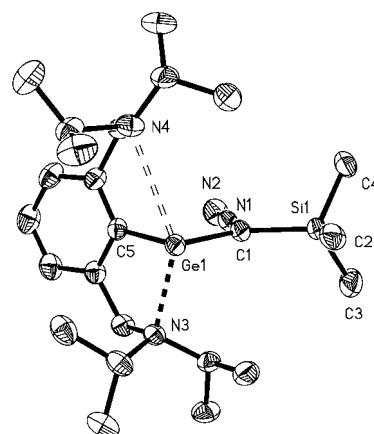
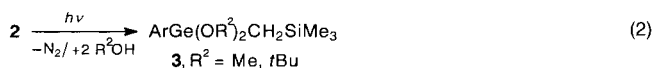


Figure 1. Molecular structure of **2** in the solid state. Selected distances [Å] and angles $^\circ$: $\text{Ge1}-\text{C5}$ 2.006(5), $\text{Ge1}-\text{C1}$ 2.02(1), $\text{Si1}-\text{C1}$ 1.85(8), $\text{Ge1}-\text{N3}$ 2.35(9), $\text{Ge1}-\text{N4}$ 3.05(3), $\text{C1}-\text{N1}$ 1.298(2), $\text{N1}-\text{N2}$ 1.146(2); $\text{C5}-\text{Ge1}-\text{C1}$ 96.84(7), $\text{C5}-\text{Ge1}-\text{N3}$ 80.46(6), $\text{C1}-\text{Ge1}-\text{N3}$ 98.94(6), $\text{N1}-\text{C1}-\text{Si1}$ 115.55(12), $\text{Ge1}-\text{C1}-\text{Si1}$ 128.0(8), $\text{Ge1}-\text{C1}-\text{N1}$ 116.33(11), $\text{N2}-\text{N1}-\text{C1}$ 178.02(10).

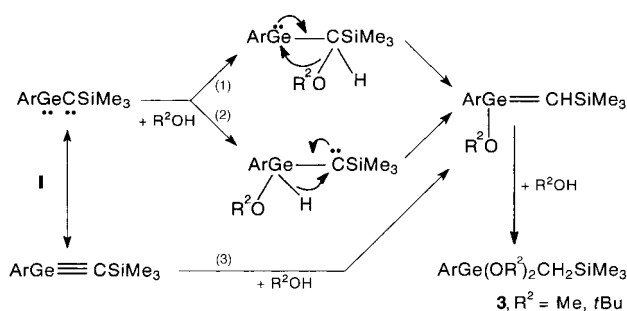
to the plane of the aryl ligand. The $\text{Ge1}-\text{C1}$ (2.02(1) Å) and $\text{C1}-\text{Si1}$ (1.85(8) Å) bond lengths are close to the normal values for σ bonds of 1.99 and 1.94 Å, respectively.^[12a] The $\text{Ge1}-\text{C1}-\text{Si1}$ angle of $128.0(8)^\circ$ is consistent with sp^2 hybridization of carbon atom C1 and a repulsive steric interaction between germanium and the SiMe_3 group.

When a solution of **2** in toluene was irradiated at -50°C and $\lambda = 300\text{ nm}$ in the absence of a trapping agent, we observed evolution of nitrogen and formation of polymeric materials. Elemental analyses of these polymers are compatible with a formula such as $(\text{ArGeCSiMe}_3)_n$. When the same irradiation was carried out in the presence of an alcohol as a trapping agent, **3** was obtained in nearly quantitative yield for $\text{R}^2 = \text{tBu}$ and in 40% yield for $\text{R}^2 = \text{Me}$ [Eq. (2)]. The



formation of **3** from the germylene–carbene species $\text{ArGe}=\text{C}=\text{SiMe}_3$ (**I**) formed by photolysis of **2** can be explained by three possible mechanisms (Scheme 2): **I** can react as a carbene (1), as a germylene (2), or as a germyne (3). All processes involve the transient formation of germene $\text{ArGe}(\text{OR}^2)=\text{CHSiMe}_3$, but routes 1 and 2 require rearrangement reactions.

Mechanism 1 can be excluded since **I** does not behave as a carbene; for example, it does not react with dienes such as 2,3-dimethylbutadiene, which is well known to react with



Scheme 2. Possible mechanisms of the trapping reaction (2).

carbenes.^[13] Moreover, kinetic studies have shown that the reactivity of alcohols towards carbenes is proportional to their acidity and that the relative reactivity of tertiary alcohols such as *t*BuOH is low.^[14] As diazogermylene **2** does not react with *t*BuOH at room temperature or with MeOH at low temperature, it does not behave as a germylene, and this rules out mechanism 2. The lack of typical carbene and germylene reactivity of **1** suggests that it is reasonable to postulate mechanism 3, in which the germyne is trapped by two equivalents of alcohol.

In conclusion, diazogermylenes, in which a carbenoid species is adjacent to a Group 14 atom bearing both a lone pair and vacant orbitals, are promising precursors to germanium–carbon triple bonds. Our results, which constitute the first chemical evidence for a germyne, contrast with *ab initio* quantum mechanical calculations of Stogner and Grev on the parent molecule HGe≡CH, which indicated that the germynylidene isomer :Ge=CH₂ is 7 kcal mol^{−1} more stable than *trans*-bent germyne, and 43 kcal mol^{−1} more stable than the linear germyne.^[15] However, our results are in accordance with the work of Apeloig and Karni in the field of silicon chemistry, who predicted that bulky substituents are expected to destabilize the vinylidene structure relative to the triple bond.^[16]

Experimental Section

All experiments were performed under a dry and oxygen-free argon atmosphere. Solvents were dried by appropriate methods. Melting points were determined in capillaries sealed under argon and are not corrected.

1: *n*-Butyllithium (4.2 mL, 1.6 M in hexane) was added dropwise to ArBr (2.0 g, 6.1 mmol) in THF (15 mL) at −78 °C, and the mixture was stirred for 20 min. A solution of GeCl₂·dioxane (1.4 g, 6.1 mmol) in THF (15 mL) was then added at the same temperature, and the reaction mixture was stirred for 30 min at room temperature. A solution of lithiotrimethylsilyldiazomethane (6.1 mmol) prepared from a solution of trimethylsilyldiazomethane (3.05 mL, 2 M in hexane) and *n*BuLi (4.2 mL, 1.6 M in hexane) in THF (15 mL) was added dropwise to the above mixture at −78 °C, and the solution was stirred at room temperature for 30 min. Solvents were removed in vacuum, and the residue was dissolved in pentane. The mixture was filtered, the solvents evaporated, and **1** was obtained as viscous oil (1.98 g, 75 % yield). ¹H NMR (400.1 MHz, C₇D₈, TMS): δ = 0.55 (s, 9H, Me₃Si), 1.11 (t, ³J(H,H) = 6.7 Hz, 12H, CH₂CH₃), 2.83 (q, ³J(H,H) = 6.7 Hz, 8H, CH₂CH₃), 3.63, 3.75 (AB system, ²J(H,H) = 14.2 Hz, 4H, CH₂), 7.10–7.30 (m, 3H); ¹³C NMR (100.6 MHz, C₇D₈, TMS): δ = 0.40 (¹J(¹³C,²⁹Si) = 26.6 Hz, CH₃Si), 9.84 (CH₂CH₃), 24.49 (CN₂), 45.31 (CH₂CH₃), 59.77 (CH₂), 124.54 (*m*-C), 127.69 (*p*-C), 145.21 (*o*-C), 156.85 (*ipso*-C); ¹⁴N NMR (28.9 MHz, C₇D₈, MeNO₂): δ = −110 (¹⁴N_α), ¹⁴N_β signal too weak to be observed; ²⁹Si NMR (39.8 MHz, C₇D₈, TMS): δ = −0.98 (Me₃Si); EI-MS (70 eV): *m/z* (%): 434 (21) [*M*⁺], 377 (2) [*M*⁺ − Et − N₂], 321 (100) [ArGe], 291 (42) [ArGe − 2Me], 220 (52) [ArGe − NEt₂ − Et], 177 (35) [ArGe − 2NEt₂]; IR (C₆D₆): ν̄ = 1994 cm^{−1} (CN₂).

2: The same procedure as for **1** was used for **2**, which was recrystallized from pentane at −20 °C (40 % yield). M.p. 78 °C (decomp); ¹H NMR (400.1 MHz, C₇D₈, TMS): δ = 0.37 (s, 9H, Me₃Si), 1.02 (d, ³J(H,H) = 7.0 Hz, 12H, CH(CH₃)₂), 1.06 (d, ³J(H,H) = 7.0 Hz, 12H, CH(CH₃)₂), 3.27 (sept, ³J(H,H) = 7.0 Hz, 4H, CH(CH₃)₂), 3.72 (s, 4H, CH₂), 7.08–7.17 (m, 3H, ArH); ¹³C NMR (100.6 MHz, C₇D₈, TMS): δ = 0.04 (CH₃Si), 20.63 (CH(CH₃)₂), 21.45 (CH(CH₃)₂), 30.15 (CN₂), 51.20 (CH(CH₃)₂), 54.36 (CH₂), 124.19 (*m*-C), 127.67 (*p*-C), 147.10 (*o*-C), 158.39 (*ipso*-C); ²⁹Si NMR (39.8 MHz, C₇D₈, TMS): δ = 0.06 (Me₃Si); EI-MS (70 eV): *m/z* (%): 490 (12) [*M*⁺], 447 (4) [*M*⁺ − *i*Pr], 419 (5) [*M*⁺ − *i*Pr − N₂], 377 (100) [ArGe]; IR (C₆D₆): ν̄ = 2001 cm^{−1} (CN₂).

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