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[8] Selected physical data for **1**: Elemental analysis for $\mathbf{1}\cdot 0.25\,H_2O$ ($C_{34}H_{42.5}Cl_2FeN_4O_{6.25}$)($M_r = 733.4$): calcd: C 55.62, H 5.79, N 7.63, Cl 9.68, Fe 7.63; found: C 55.45, H 5.87, N 7.64, Cl 9.75, Fe 7.68; ESI/MS(CH_3CN): m/z: 693 (100%) $[FeLCl]^+$; UV/Vis (CH_3CN): λ_{max} (ε, $M^{-1}cm^{-1}$): 415 nm (1050). Crystal data of $\mathbf{1}\cdot CH_3CN$: $C_{36}H_{45}Cl_2FeN_5O_6$, $M_r = 770.52$, triclinic, space group $P\bar{1}$, $a = 13.1459(2)$, $b = 15.5146\ (2)$, $c = 18.5430\ (2)$ Å, $\alpha = 92.19(1)$, $\beta = 98.22(1)$, $\gamma = 99.93(1)^\circ$, $V = 3679.34(8)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.391\ g\,cm^{-3}$, $\mu = 0.607\ mm^{-1}$, $\lambda = 0.71073$ Å, direct methods, $R[I > 2\sigma(I)] = 0.0305$ for 12229 independent reflections of the 17177 collected, R(all data) = 0.046. Selected physical data for **2**: Elemental analysis for $\mathbf{2}(ClO_4)_2\cdot 3\,H_2O$ ($C_{34}H_{48}Cl_2FeN_4O_{17}$)($M_r = 911.3$): calcd: C 44.80, H 5.26, N 6.15, Cl 7.78, Fe 6.15; found: C 44.80, H 5.44, N 6.16, Cl 8.22, Fe 5.75; ESI/MS (CH_3CN): m/z: 757 (100%) $[FeLClO_4]^+$; UV/Vis (CH_3CN): λ_{max} (ε, $M^{-1}cm^{-1}$): 377 nm (1700). Suitable crystals for an X-ray analysis were obtained after a metathesis of ClO_4 for PF_6 anions. Crystal data of $\mathbf{2}(PF_6)_2\cdot 2.5\,CH_3CN\cdot 0.25\,CH_3OH\cdot 0.5\,H_2O$: $C_{43.25}H_{57.5}F_{12}P_2FeN_{8.5}O_{6.75}$, $M_r = 1144.22$, triclinic, space group $P\bar{1}$, $a = 13.3988(9)$, $b = 14.5835(9)$, $c = 27.8533\ (17)$ Å, $\alpha = 98.096(1)$, $\beta = 94.746(1)$, $\gamma = 94.264(1)^\circ$, $V = 5349.4(6)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.421\ g\,cm^{-3}$, $\mu = 0.437\ mm^{-1}$, $R[I > 2\sigma(I)] = 0.0748$ for 24469 independent reflections of the 34761 collected, R(all data) = 0.1708. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-146454 (**1**) and CCDC-146455 ($\mathbf{2}(PF_6)_2$). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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[10] The resulting solution was concentrated and diluted in water in the presence of excess dithionite and bathophenanthroline. The organic material was extracted from the solution by using dichloromethane and choloroform.

[11] Comparisons between ^1H and ^{13}C NMR spectra of L and LOH allowed us to unambiguously attribute the inserted oxygen position. In fact, the signal at $\delta = 6.63$ corresponding to the *o*-H for L is replaced by two signals at $\delta = 6.63$ and 6.42 in a 2:1 ratio for LOH. A similar trend is observed in the ^{13}C NMR spectrum (for the *o*-C of the phenyl ring signals appear at $\delta = 108.5$ and 105.5 for LOH, but only at $\delta = 105.0$ for L). ESI-MS for LOH (CH_2Cl_2; positive-ion mode): m/z: 619 (100%) for $[LOH + H^+]$.

[12] The HPLC titration has been carried out on authentic pure samples of L, L1, and LOH obtained by extraction of the reaction mixture at higher concentration. Other minor products have been detected but their structures remain unknown.

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[14] The reaction mixture contains both mononuclear Fe^{II} and Fe^{III} L and L1 complexes.

[15] ^1H NMR (300 MHz, CD_3CN, 25 °C): $\delta = 2.66$ (m, 4H; NCH_2CH_2N), 3.52 (s, 2H; CH_2Bz), 3.62 (s, 3H; OCH_3), 3.67 (s, 2H; CH_2py), 3.69 (s, 6H; OCH_3), 3.72 (s, 2H; CH_2py), 6.63 (s, 2H; $o\text{-}H_{Ph}$); 7.13 (td, 2H; $m\text{-}H_{py}$); 7.23 (d, 1H; $p\text{-}H_{py}$), 7.43 (d, 1H; $p\text{-}H_{py}$), 7.61 (t, 2H; $m\text{-}H_{py}$), 8.41 (dd, 2H, $o\text{-}H_{py}$). ESI/MS (CH_2Cl_2; positive-ion mode): m/z: 423 (100%) for $[L1 + H^+]$.

[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/H_2O_2 1/1100/10 in acetonitrile inside a glove box (dioxygen content less than 1 ppm) using syringe pump conditions; delivering time = 30 min [complex] = 0.7 mM.

[18] The isotope ratio in cyclohexanol has been analyzed by GC/MS on a reaction mixture directly after reaction. Cyclohexanol was not labeled in the presence of ^{18}O water under standard conditions.

[19] No 1,2-cyclohexanediol was detected.

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[21] Notably, $[(bpmen)Fe^{II}Cl_2]/H_2O_2$ showed the same stereoselectivity, selectivity, and catalytic properties as complex **1** (bpmen = *N,N'*-dimethyl-*N,N'*-bis(2-pyridylmethyl)ethane-1,2-diamine). Thus, the concomitant formation of $[Fe(LO)Cl_2]$ is not responsible for the poor catalytic properties.

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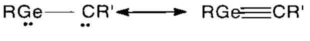
various other methods.[4] Germaisocyanides :Ge≡NR have only been detected by photoelectron spectroscopy,[5] whereas in coordination chemistry, stable transition metal germylyne complexes have been reported and structurally characterized since 1996.[6] No triple bond to tin has yet been described.

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 RGe≡CR′ from a germylene–carbene structure (Scheme 1).



$$R\ddot{\mathrm{Ge}}-\ddot{\mathrm{C}}R' \longleftrightarrow R\mathrm{Ge}\equiv \mathrm{C}R'$$

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

Coupling reactions between germylenes (or stannylenes) and carbenes that provide convenient access to Ge=C and Sn=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. Diazogermylenes RGeC(N$_2$)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 diazogermylenes ArGeC(N$_2$)SiMe$_3$ and an initial study of their photochemical behavior.

The 2,6-bis[(dialkylamino)methyl]phenyl groups (R$^1_2$NCH$_2$)$_2$-C$_6$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 (R^1 = Me, Et)[10a–c] as well as a chlorostannylene (R^1 = Me).[10d]

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

$$\mathrm{ArBr} \xrightarrow[\mathrm{THF}]{n\mathrm{BuLi}} \mathrm{ArLi} \xrightarrow[\mathrm{THF}]{:\mathrm{GeCl_2}} \mathrm{Ar\ddot{G}eCl} \xrightarrow[\mathrm{THF/C_6H_{14}}]{\mathrm{Me_3SiC(N_2)Li}} \mathrm{Ar\ddot{G}eC(N_2)SiMe_3} \qquad (1)$$

$$\mathrm{Ar} = 2,6\text{-}(\mathrm{R^1_2NCH_2})_2\mathrm{C_6H_3} \qquad \mathrm{R^1} = \mathrm{Et}\text{: } \mathbf{1},\ i\mathrm{Pr}\text{: } \mathbf{2}$$

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$_2$N*i*Pr$_2$ side chain. The Ge1–N3 distance of 2.35(9) Å is, as expected, longer than the a normal Ge–N σ bond (1.92 Å[12a]) but much shorter than the sum of the van der Waals radii (3.74 Å[12b]). The Ge–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 Ge1–C1 bond, which is oriented almost orthogonal (96.8°) to the plane of the aryl ligand. The Ge1–C1 (2.02(1) Å) and C1–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 Ge1-C1-Si1 angle of 128.0(8)° is consistent with sp^2 hybridization of carbon atom C1 and a repulsive steric interaction between germanium and the SiMe$_3$ group.

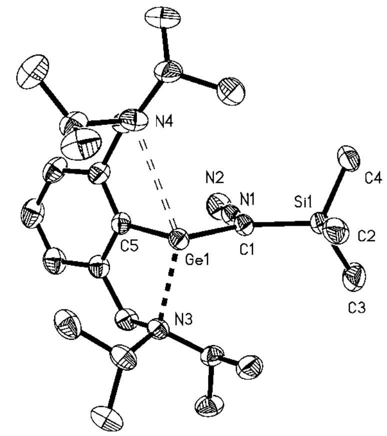


Figure 1. Molecular structure of **2** in the solid state. Selected distances [Å] and angles [°]: Ge1-C5 2.006(5), Ge1-C1 2.02(1), Si1-C1 1.85(8), Ge1-N3 2.35(9), Ge1-N4 3.05(3), C1-N1 1.298(2), N1-N2 1.146(2); C5-Ge1-C1 96.84(7), C5-Ge1-N3 80.46(6), C1-Ge1-N3 98.94(6), N1-C1-Si1 115.55(12), Ge1-C1-Si1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

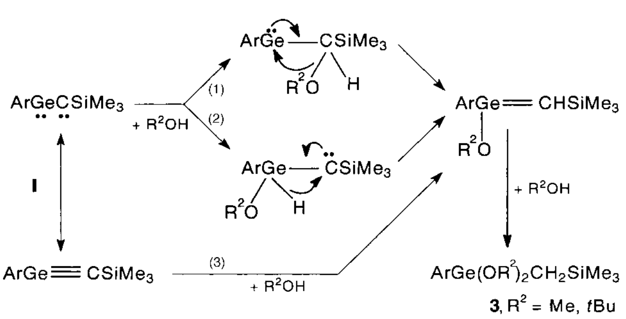
When a solution of **2** in toluene was irradiated at −50 °C and $\lambda = 300$ nm in the absence of a trapping agent, we observed evolution of nitrogen and formation of polymeric materials. Elemental analyses of these polymers are compatible with a formula such as (ArGeCSiMe$_3$)$_n$. When the same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

$$\mathbf{2} \xrightarrow[-\mathrm{N_2}/+2\,\mathrm{R^2OH}]{h\nu} \mathrm{ArGe(OR^2)_2CH_2SiMe_3} \qquad (2)$$

$$\mathbf{3},\ \mathrm{R^2} = \mathrm{Me},\ t\mathrm{Bu}$$

formation of **3** from the germylene–carbene species Ar$\ddot{\mathrm{G}}$e–$\ddot{\mathrm{C}}$-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 ArGe(OR^2)=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 **I** 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 $HGe{\equiv}CH$, which indicated that the germavinylidene isomer $:Ge{=}CH_2$ 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 $GeCl_2 \cdot$ 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, C_7D_8, TMS): $\delta = 0.55$ (s, 9H, Me_3Si), 1.11 (t, $^3J(H,H) = 6.7$ Hz, 12H, CH_2CH_3), 2.83 (q, $^3J(H,H) = 6.7$ Hz, 8H, CH_2CH_3), 3.63, 3.75 (AB system, $^2J(H,H) = 14.2$ Hz, 4H, CH_2), 7.10–7.30 (m, 3H); ^{13}C NMR (100.6 MHz, C_7D_8, TMS): $\delta = 0.40$ ($^1J(^{13}C,^{29}Si) = 26.6$ Hz, CH_3Si), 9.84 (CH_2CH_3), 24.49 (CN_2), 45.31 (CH_2CH_3), 59.77 (CH_2), 124.54 (*m*-C), 127.69 (*p*-C), 145.21 (*o*-C), 156.85 (*ipso*-C); ^{14}N NMR (28.9 MHz, C_7D_8, $MeNO_2$): $\delta = -110$ ($^{14}N_\alpha$), $^{14}N_\beta$ signal too weak to be observed; ^{29}Si NMR (39.8 MHz, C_7D_8, TMS): $\delta = -0.98$ (Me_3Si); EI-MS (70 eV): *m*/*z* (%): 434 (21) [$M^{\cdot+}$], 377 (2) [$M^{\cdot+} - Et - N_2$], 321 (100) [ArGe], 291 (42) [ArGe – 2Me], 220 (52) [$ArGe - NEt_2 - Et$], 177 (35) [$ArGe - 2NEt_2$]; IR (C_6D_6): $\tilde{\nu} = 1994$ cm^{-1} (CN_2).

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, C_7D_8, TMS): $\delta = 0.37$ (s, 9H, Me_3Si), 1.02 (d, $^3J(H,H) = 7.0$ Hz, 12H, $CH(CH_3)_2$), 1.06 (d, $^3J(H,H) = 7.0$ Hz, 12H, $CH(CH_3)_2$), 3.27 (sept, $^3J(H,H) = 7.0$ Hz, 4H, $CH(CH_3)_2$), 3.72 (s, 4H, CH_2), 7.08–7.17 (m, 3H, ArH); ^{13}C NMR (100.6 MHz, C_7D_8, TMS): $\delta = 0.04$ (CH_3Si), 20.63 ($CH(CH_3)_2$), 21.45 ($CH(CH_3)_2$), 30.15 (CN_2), 51.20 ($CH(CH_3)_2$), 54.36 (CH_2), 124.19 (*m*-C), 127.67 (*p*-C), 147.10 (*o*-C), 158.39 (*ipso*-C); ^{29}Si NMR (39.8 MHz, C_7D_8, TMS): $\delta = 0.06$ (Me_3Si); EI-MS (70 eV): *m*/*z* (%): 490 (12) [$M^{\cdot+}$], 447 (4) [$M^{\cdot+} - i$Pr], 419 (5) [$M^{\cdot+} - i\text{Pr} - N_2$], 377 (100) [ArGe]; IR (C_6D_6): $\tilde{\nu} = 2001$ cm^{-1} (CN_2).

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[11] Crystal data for **2**: $C_{24}H_{44}GeN_4Si$, $M_r = 489.31$, monoclinic, space group $P2_1/c$, $a = 10.3936(3)$, $b = 10.8900(3)$, $c = 24.2005(8)$ Å, $\beta = 99.247(1)°$, $V = 2703.6(1)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.202$ Mg m^{-3}, $F(000) = 1048$, $\lambda = 0.71073$ Å, $T = 193(2)$ K, $\mu(Mo_{K\alpha}) = 1.194$ mm^{-1}, crystal dimensions $0.1 \times 0.6 \times 0.8$ mm, $2.53 \leq \theta \leq 30.49°$; 22744 reflections (8204 independent, $R_{int} = 0.0469$) were collected at low temperature on an oil-coated shock-cooled crystal on a Bruker-AXS CCD 1000 diffractometer. A semi-empirical absorption correction was employed ($T_{min} = 0.546246$, $T_{max} = 1.000000$).[17] The structure was solved by direct methods (SHELXS-97)[18], and 340 parameters were refined by the least-squares method on F^2.[19] Maximum residual electron density: 1.068 e Å^{-3}, $R1$ (for $F > 2\sigma(F)) = 0.0375$ and $wR2 = 0.0990$ (all data) with $R1 = \Sigma|F_o| - |F_c|/\Sigma|F_o|$ and $wR2 = (\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2)^{0.5}$. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-149434. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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