



## Reactivity of a germa-alkyne: Evidence for a germanone intermediate in the hydrolysis and alcoholysis processes

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### ABSTRACT

The formation of a new transient germa-alkyne  $\text{Ar-Ge}\equiv\text{C-SiMe}_3$  [Ar = 2,4-di-*tert*-butyl-6-(diisopropylaminomethyl)phenyl] is achieved by photolysis of the corresponding trimethylsilyldiazomethylgermylene  $\text{ArGeC(N}_2\text{)SiMe}_3$  (**2**). The germa-alkyne is characterized by trapping reactions with  $\text{H}_2\text{O}$  and an equimolar mixture of *tert*-butanol and water. The respective adducts, the gem-germanediol **5** and the alkoxygermanol **4** have been fully characterized by spectroscopic methods. A study of the mechanism is proposed and in both cases, the addition involves the transient formation of a germanone. The structures of **2** and **5** are determined by single-crystal X-ray diffraction.

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### 1. Introduction

For nearly 30 years, in organometallic main group chemistry, unsaturated compounds with metal-carbon multiple bonds present a particular interest. This is in relation with their chemical reactivity which is quite different and much greater than their corresponding organic analogues. If metal<sub>14</sub>-alkenes such as silenes  $\text{>Si=C<}$  [1], germenes  $\text{>Ge=C<}$  [2] and stannenes  $\text{>Sn=C<}$  [3] are now numerous, metalla-alkynes of general formula  $\text{-M}\equiv\text{C-}$  (M = Si, Ge, Sn) are still rare or unknown. Indeed, only one germa-alkyne [4] and two stanna-alkynes [5] are described in the literature. These compounds still have a short lifetime and are characterized by trapping reactions.

In this paper we present the synthesis of a new germa-alkyne and many aspects of its chemical reactivity. A study of the mechanisms of the hydrolysis and alcoholysis reactions is investigated.

### 2. Results and discussion

#### 2.1. Synthesis of the germa-alkyne $\text{Ar-Ge}\equiv\text{C-SiMe}_3$ **3** [Ar = 2,4-di-*tert*-butyl-6-(diisopropylaminomethyl)phenyl]

Based on our previously described synthetic pathway [4], the synthesis of the germa-alkyne involves successive reactions. First

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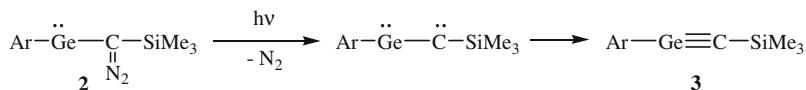
E-mail address: [mazieres@chimie.ups-tlse.fr](mailto:mazieres@chimie.ups-tlse.fr) (S. Mazières).

the corresponding chlorogermylene **1** (of general formula:  $\text{ArGeCl}$ ) is generated and leads by substitution reaction with the lithium salt of the trimethylsilyldiazomethane to the substituted-diazomethylgermylene  $\text{ArGeC(N}_2\text{)SiMe}_3$  **2**. The latter is decomposed by photolysis to generate the corresponding germylene-carbene which can be written in a contribution form as a germa-alkyne **3** (Scheme 1).

#### 2.1.1. Synthesis and characterization of the chlorogermylene **1**

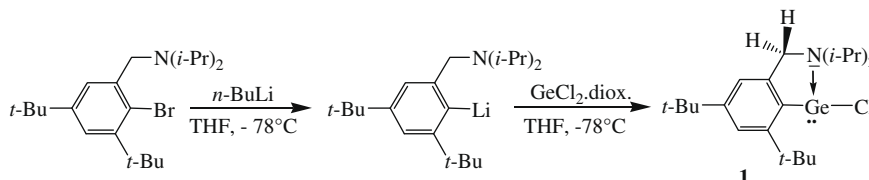
The chlorogermylene **1** is obtained by reaction of the lithium derivative  $\text{ArLi}$  [Ar = 2,4-di-*tert*-butyl-6-(diisopropylaminomethyl)phenyl] with the dichlorogermylene · dioxane complex, as summarized in Scheme 2.

The  $^1\text{H}$  NMR spectrum of **1** is characteristic of such a structure, especially concerning the signal relative to the diastereotopic benzylic hydrogen atoms, which appears as an AX system. The chirality of the germanium atom, which is enhanced by the intramolecular coordination  $\text{N} \rightarrow \text{Ge}$  explains the non-equivalence of these hydrogen atoms. Also by the  $^{13}\text{C}$  NMR analysis we can notice that the isopropyl groups are not equivalent and generate twice as many signals. We grew crystals of **1**, but unfortunately, with insufficient quality for a satisfactory X-ray analysis (see Supplementary materials). Nevertheless, a few interesting data can be extracted and the main feature is the strong donation of the nitrogen to the germanium center ( $d_{\text{Ge-N}} = 2.153 \text{ \AA}$ ). This is in relation with the marked withdrawing effect of the chlorine atom. As expected, this coordination causes the lengthening of the Ge-Cl bond (2.338 Å) and thus increases the leaving ability of the chlorine.

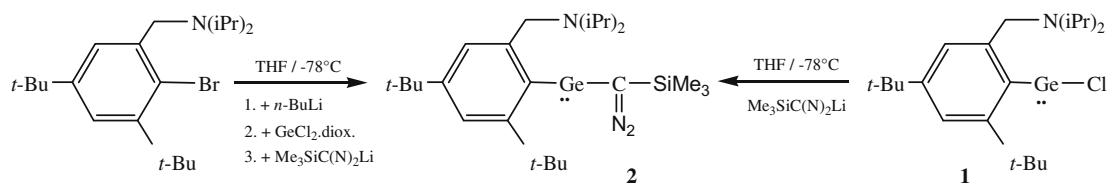


Ar = 2,4-di-*tert*-butyl-6-(diisopropylaminomethyl)phenyl

Scheme 1.



Scheme 2.



Scheme 3.

Indeed, easy nucleophilic substitutions on the germanium atom can be carried out, such as the reaction with the trimethylsilyldiazomethane anion which leads to the diazomethylgermylene **2** with good yields (Scheme 3).

### 2.1.2. Synthesis and characterization of the diazomethylgermylene **2**

The synthesis of **2** can be realized from **1** by reaction with the trimethylsilyldiazomethane anion or can also be brought about directly by a one pot reaction starting from the brominated ligand (Scheme 3).

As for **1**, the  $^1\text{H}$  NMR spectrum of **2** shows a characteristic AB system for the benzylic protons. The presence of the diazo moiety is evidenced first by  $^{13}\text{C}$  NMR with a signal at 28.83 ppm for the diazo carbon, which is in accordance with the value previously found for a similar compound [4]. Also the vibration observed in the infrared analysis ( $\bar{\nu}_{\text{CN}_2} = 2002.9 \text{ cm}^{-1}$ ) and the UV absorption ( $n-\pi^*$  transition at 366 nm,  $\epsilon: 126 \text{ L mol}^{-1} \text{ cm}^{-1}$ ) are in agreement with the diazo structure (see Fig. 1).

X-ray analysis of **2** shows a monomeric structure in the solid state with a strong interaction between the germanium and the nitrogen atom of the side chain. Indeed, the Ge–N(3) distance (2.252 Å) is appreciably shorter than the sum of van der Waals radii (3.74 Å) [6] but longer than a usual germanium–nitrogen  $\sigma$  bond (1.84 Å) [7]. Ge–C(1) and Ge–C(2) bonds are nearly in an orthogonal position (97°); Ge–C(1) (2.031 Å) and C(1)–Si (1.846 Å) bond lengths are close to the standard values for these corresponding  $\sigma$  bonds, 1.94 and 1.85 Å, respectively [7]. The angle Ge–C(1)–Si (126.6°) suggests an  $\text{sp}^2$  hybridization for the C(1) carbon atom and is slightly increased by the steric repulsion around the germanium atom on one side and by the trimethylsilyl group on the other side.

Moreover the examination of the main data from the previously described diazogermylene [4], with two side arms on the aryl group, allows an interesting comparison with **2** concerning these two kinds of ligand (types I and II) (see Fig. 2).

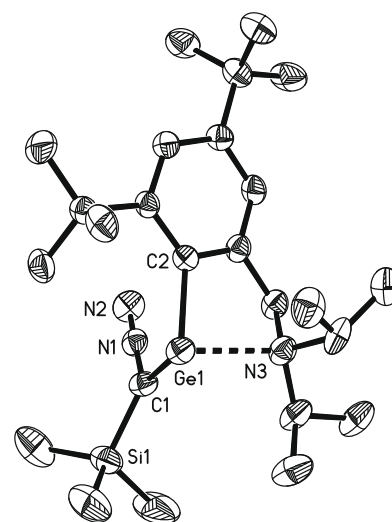


Fig. 1. Molecular structure of **2** in the solid state. Thermal ellipsoids are at the 50% probability level. Hydrogen atoms are omitted for clarity.

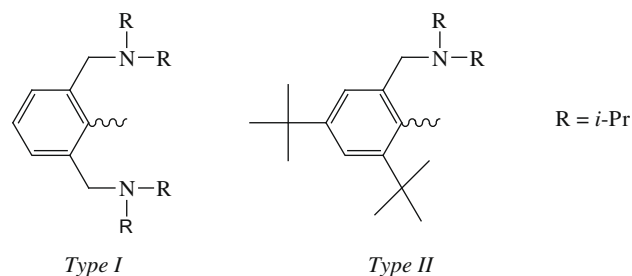


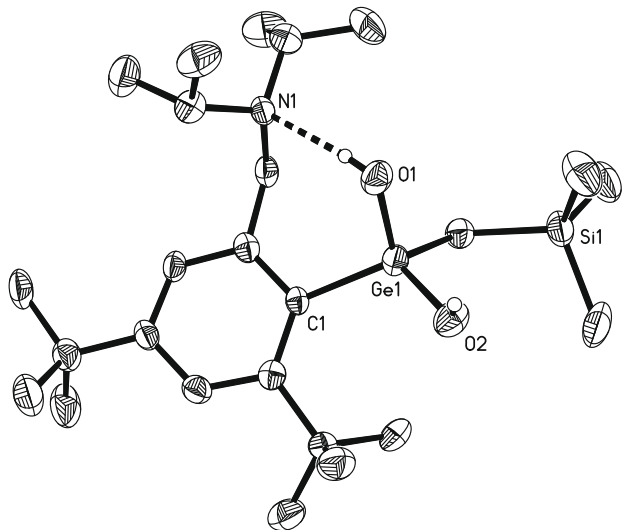
Fig. 2. Ligands.

This kind of *type II* ligand (with R = Me) was introduced by Yoshifuji and coworkers in 1994 [8a] and used later by Jutzi in germanium chemistry [8b]. This ligand combines the steric features of a supermesityl group and the electronic properties of the *o*-((diisopropylamino)methyl)phenyl system. On the other hand, *type I* which is known as a pincer ligand combines mainly the electronic effects of the two side arms.

The most significant difference of these ligands (Ar) is the stronger intramolecular coordination occurring in *type II*. This can be related to the germanium–nitrogen distances observed for the corresponding diazo compounds  $\text{ArGeC}(\text{N}_2)\text{SiMe}_3$ . These distances are much longer in the diazocompound using the *type I* ligand (Ge–N: 2.359 and 3.05 Å) where the two nitrogen atoms interact successively with the germanium center, leading to a dynamic system [4]. In contrast, the Ge–N bond length (2.252 Å) observed in **2** shows a strong interaction, indicating a static system where the germanium is in constant coordination with the nitrogen. This difference in structure will lead to a different chemical behavior.

### 2.1.3. Photochemical decomposition of diazomethylgermylene **2**

The photolysis is performed in toluene at room temperature with a Medium-Pressure mercury lamp (Oriel Company) with a maximum wavelength of 365 nm and causes the expected dinitrogen evolution. A complete decomposition of **2** is observed in less than 30 min for a standard experiment (see Section 4). When the photolysis is monitored without a trapping reagent, we observe



**Fig. 3.** Molecular structure of **5** in the solid state. Thermal ellipsoids are at the 50% probability level. Hydrogen atoms are omitted for clarity.

the formation of solid polymeric materials of general formula  $(\text{ArGeCSiMe}_3)_n$ . The total disappearance of **2** is confirmed by NMR analysis and the  $^1\text{H}$  NMR spectrum shows broad signals characteristic of such polymeric structures. Otherwise, when this photolysis is performed at low temperature ( $-50^\circ\text{C}$ ) we do not observe any evolution of nitrogen. It is interesting to notice that a blue emission occurs during the irradiation. This phenomenon does not take place at room temperature, indicating that it is due to phosphorescence. A thermal activation barrier should be involved in this photochemical process, and this mainly tells us that it is not possible to generate such unsaturated species at low temperature.

### 2.1.4. Photochemical decomposition with a trapping reagent

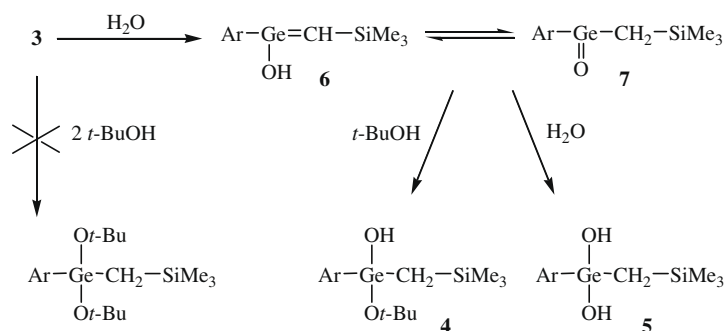
The same photolysis is performed in a toluene solution and in presence of an excess of 2-methylpropan-2-ol (*tert*-butyl alcohol) as a trapping agent, at room temperature. The choice of such a tertiary alcohol is justified because it is non-reactive towards the diazocompound **2**. Surprisingly and contrary to what was already described [4], we do not observe the formation of the expected dialkoxygermane  $\text{ArGe}(\text{O}t\text{-Bu})_2\text{CH}_2\text{SiMe}_3$  resulting from the addition of two equivalents of *tert*-butyl alcohol to the germanium–carbon triple bond in relation with its polarity  $\text{Ge}^{\delta+}\text{-C}^{\delta-}$ . In our case, only polymeric materials are obtained and the trapping agent does not play any role.

Next we realized the decomposition of **2** in a toluene solution in the presence of *tert*-butyl alcohol in excess and a stoichiometric amount (1 equiv.) of water. We checked beforehand that in our experimental conditions (toluene solution at room temperature)  $\text{H}_2\text{O}$  does not react with **2**. Under these conditions we observe the formation of the alkoxygermanol  $\text{ArGe}(\text{O}t\text{-Bu})(\text{OH})\text{CH}_2\text{SiMe}_3$  **4** in nearly quantitative yield. The same reaction, performed in the presence of *tert*-butyl alcohol but with 2 equiv. of water, leads almost exclusively to the *gem*-germanediol  $\text{ArGe}(\text{OH})_2\text{CH}_2\text{SiMe}_3$  **5**.

Compound **4** appears as a waxy material, impossible to crystallize, but it is unambiguously identified by usual spectroscopic methods (see Section 4). On the other hand, single crystals of **5** are obtained allowing an X-ray analysis (see Fig. 3).

Concerning **5** which has a dimeric structure in the solid state, we can observe that the coordination  $\text{N} \rightarrow \text{Ge}$  disappears and is replaced by an hydrogen bond between the nitrogen atom of the arm and the hydrogen atom of a hydroxyl moiety ( $\text{N}\cdots\text{H}(1) = 1.979 \text{ \AA}$ ). This hydrogen bonding is evidenced by a  $\text{N}\cdots\text{O}$  distance of 2.712 Å, which indicates a quite strong  $\text{N}\cdots\text{H}$  interaction in the solid state [9]. This intramolecular bond leads to a decrease of the angle  $\text{C}(1)\text{-Ge-O}(1)$  ( $106.04^\circ$ ) in the seven membered pseudo-cycle compared to the external angle  $\text{C}(1)\text{-Ge-O}(2)$  ( $115.16^\circ$ ).

Such stable *gem*-germanediols are interesting compounds and only a few are reported in the literature [10 and references therein].



**Scheme 4.**

### 2.1.5. Study of the mechanism of alcoholysis and hydrolysis reactions of the germa-alkyne

The photolysis of trimethylsilyldiazomethylgermylene **2** efficiently generates the corresponding germylene–carbene which can be considered as a contributing structure of a germa-alkyne **3** (as shown in Scheme 1), after evolution of dinitrogen.

Our experimental results show that *tert*-butyl alcohol does not react with the germa-alkyne **3** and the presence of water is necessary to observe a reaction. So we can postulate that the first step of this reaction is the addition of H<sub>2</sub>O on the germanium–carbon triple bond. This addition can be explained by a better reactivity of H<sub>2</sub>O compared to the tertiary alcohol *t*-BuOH, relative to their corresponding acidity. This electrophilic addition leads to the hydroxygermene **6** or its keto-tautomer **7**. Germanones, which can be considered as heavy analogues of ketones, are known to be extremely reactive intermediates [10 and references therein]. And it is known that the reaction of germa-alkenes are quite slow with tertiary alcohols, mainly due to the acidity which plays a dominant role [11]. In our process, **7** could then react with *t*-BuOH to lead to the alkoxygermanol **4** or with H<sub>2</sub>O to generate the *gem*-germanediol **5** (Scheme 4).

A similar mechanism was postulated by Tokitoh and coll. for the hydrolysis and alcoholysis reactions of a digermene [12]. The authors, using theoretical calculations, found for their Dmp model (Dmp = 2,6-dimethylphenyl) that the germanone (DmpGe(O)-GeH<sub>2</sub>Dmp) was 9.9 kcal/mol more stable than the enol tautomer. In accordance with these results, and due to the fact that **3** does not react directly with *tert*-butyl alcohol, it seems reasonable to postulate that in our case the germanone **7** is the active intermediate in the hydrolysis and alcoholysis of the germa-alkyne.

## 3. Conclusion

The synthesis of the germyne Ar-Ge≡C-SiMe<sub>3</sub> **3** [Ar = 2,4-*tert*-butyl-6-(diisopropylaminomethyl)phenyl], as well as its chlorogermene ArGeCl and diazogermene ArGeC(N<sub>2</sub>)SiMe<sub>3</sub> precursors, have been reported. This new organometallic alkyne was evidenced by trapping reactions with water and *tert*-butyl alcohol. Using different stoichiometric amounts of reactants, it was demonstrated that the active intermediate is the germanone ArGe(O)CH<sub>2</sub>-SiMe<sub>3</sub> resulting from the electrophilic addition of H<sub>2</sub>O onto the germanium–carbon triple bond. The *gem*-germanediol and the alkoxygermanol obtained arose respectively from the subsequent addition of H<sub>2</sub>O or *t*-BuOH onto the germanone intermediate.

These results show that unsaturated organometallic compounds such as germa-alkynes or germanones can lead to similar reactions to those of their corresponding organic compounds, but present a very much higher reactivity.

## 4. Experimental

### 4.1. General methods

All reactions were carried out under an atmosphere of purified argon using standard Schlenk techniques. Tetrahydrofuran, diethyl ether, toluene, *n*-pentane were purified by distillation from sodium/benzophenone ketyl. Infrared spectra were recorded with a Perkin-Elmer FT-IR 1600 spectrometer. The <sup>1</sup>H (300.1 MHz), <sup>13</sup>C (75.4 MHz) and <sup>29</sup>Si (59.6 MHz) NMR spectra were recorded on the spectrometer Bruker Avance 300. Nucleus, frequency and solvent were indicated for each compound. Chemical shifts are reported in ppm units (parts per million) downfield from tetramethylsilane (<sup>1</sup>H, <sup>13</sup>C, <sup>29</sup>Si). Melting points were determined using sealed argon purged capillaries with a Leitz Biomed 50 melting point apparatus. Microanalyses were performed at the Analytical

Laboratory of the Laboratoire de Chimie de Coordination, Toulouse, France. ArBr was prepared as for the methyl derivative described in the literature [13].

### 4.2. Synthesis of 1-bromo-2,4-di-*tert*-butyl-6-(diisopropylaminomethyl)benzene

A solution of diisopropylamine (74 mL, 0.41 mol) and 2-bromo-1-bromomethyl-3,5-di-*tert*-butylbenzene (68.42 g, 0.19 mol) in toluene (400 mL) was refluxed for 48 h. Diisopropylammonium bromide was eliminated by filtration then the solvent was removed in vacuum leading to yellow oil which was purified by distillation.

(64.8 g, 0.17 mol, 90% yield); Eb: 122 °C/0.2 mmHg; <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>), δ (ppm): 0.96 (d, <sup>3</sup>J<sub>H/H</sub> = 6.5 Hz, 12H, CH(CH<sub>3</sub>)<sub>2</sub>), 1.36 (s, 9H, C(CH<sub>3</sub>)<sub>3</sub>), 1.63 (s, 9H, C(CH<sub>3</sub>)<sub>3</sub>), 2.93 (sept, <sup>3</sup>J<sub>H/H</sub> = 6.5 Hz, 2H, CH(CH<sub>3</sub>)<sub>2</sub>), 3.89 (s, 2H, CH<sub>2</sub>), 7.52 (d, <sup>4</sup>J<sub>H/H</sub> = 3.2 Hz, 1H, H<sub>5</sub>), 7.98 (d, <sup>4</sup>J<sub>H/H</sub> = 3.2 Hz, 1H, H<sub>3</sub>); <sup>13</sup>C NMR (C<sub>6</sub>D<sub>6</sub>), δ (ppm): 20.68 (CH(CH<sub>3</sub>)<sub>2</sub>), 30.16 (C(CH<sub>3</sub>)<sub>3</sub>), 31.26 (C(CH<sub>3</sub>)<sub>3</sub>), 34.71 (C(CH<sub>3</sub>)<sub>3</sub>), 37.21 (C(CH<sub>3</sub>)<sub>3</sub>), 48.63 (CH(CH<sub>3</sub>)<sub>2</sub>), 51.02 (CH<sub>2</sub>), 121.30 (1-aryl-C), 123.09 (5-aryl-C), 125.65 (3-aryl-C), 142.94 (2-aryl-C), 146.80 (4-aryl-C), 148.82 (6-aryl-C); SM-IE (70 eV), *m/z* (%): 381 (M<sup>+</sup>, 17), 366 (M<sup>+</sup>-Me, 50), 281 (M<sup>+</sup>-N(iPr)<sub>2</sub>, 100).

### 4.3. Synthesis of 1-chloro-1-[4,6-di-*tert*-butyl-2-(diisopropylaminomethyl)phenyl]germylene (**1**) (ArGeCl)

A solution of *n*-butyllithium (1.1 mL, 1.75 mmol, 1.6 M in hexane) was added dropwise to a solution of 1-bromo-2,4-di-*tert*-butyl-6-(diisopropylaminomethyl)benzene (0.61 g, 1.59 mmol) in THF (6 mL) at (-78 °C). The brown mixture was stirred for 30 min then added dropwise to a solution of GeCl<sub>2</sub>-dioxane (0.37 g, 1.59 mmol) in THF at -78 °C. The mixture was allowed to warm to room temperature. Solvents were removed under vacuum to generate crude **1** which was dissolved in pentane 20 mL. After filtration through Celite the pentane was removed leading to a yellow solid.

(0.51 g, 1.25 mmol, 79% yield); m.p.: 168–169 °C; <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>), δ (ppm): 0.75 (d, <sup>3</sup>J<sub>H/H</sub> = 6.7 Hz, 3H, CH(CH<sub>3</sub>)<sub>2</sub>), 0.80 (d, <sup>3</sup>J<sub>H/H</sub> = 9.1 Hz, 3H, CH(CH<sub>3</sub>)<sub>2</sub>), 0.82 (d, <sup>3</sup>J<sub>H/H</sub> = 6.7 Hz, 3H, CH(CH<sub>3</sub>)<sub>2</sub>), 1.32 (d, <sup>3</sup>J<sub>H/H</sub> = 6.7 Hz, 3H, CH(CH<sub>3</sub>)<sub>2</sub>), 1.35 (s, 9H, C(CH<sub>3</sub>)<sub>3</sub>), 1.62 (s, 9H, C(CH<sub>3</sub>)<sub>3</sub>), 3.04 (sept, <sup>3</sup>J<sub>H/H</sub> = 6.7 Hz, 1H, CH(CH<sub>3</sub>)<sub>2</sub>), 3.77–4.57 (AX system, <sup>2</sup>J<sub>H/H</sub> = 15.0 Hz, 2H, CH<sub>2</sub>N), 4.08 (sept, <sup>3</sup>J<sub>H/H</sub> = 6.7 Hz, 1H, CH(CH<sub>3</sub>)<sub>2</sub>), 7.02 (d, <sup>4</sup>J<sub>H/H</sub> = 3.4 Hz, 1H, H<sub>5</sub>), 7.48 (d, <sup>4</sup>J<sub>H/H</sub> = 3.4 Hz, 1H, H<sub>3</sub>); <sup>13</sup>C NMR (C<sub>6</sub>D<sub>6</sub>), δ (ppm): 18.16 (CH(CH<sub>3</sub>)<sub>2</sub>), 20.61 (CH(CH<sub>3</sub>)<sub>2</sub>), 20.97 (CH(CH<sub>3</sub>)<sub>2</sub>), 22.69 (CH(CH<sub>3</sub>)<sub>2</sub>), 31.35 (C(CH<sub>3</sub>)<sub>3</sub>), 33.22 (C(CH<sub>3</sub>)<sub>3</sub>), 34.59 (C(CH<sub>3</sub>)<sub>3</sub>), 37.47 (C(CH<sub>3</sub>)<sub>3</sub>), 51.17 (CH(CH<sub>3</sub>)<sub>2</sub>), 57.47 (CH(CH<sub>3</sub>)<sub>2</sub>), 60.23 (CH<sub>2</sub>), 117.67 (3-aryl-C), 120.69 (5-aryl-C), 146.79 (2-aryl-C), 150.65 (4-aryl-C), 155.43 (6-aryl-C), 156.56 (1-aryl-C); EI-MS (70 eV), *m/z* (%): 411 (M<sup>+</sup>, 85), 376 (M<sup>+</sup>-Cl, 90), 368 (M<sup>+</sup>-iPr, 100), 354 (M<sup>+</sup>-*t*Bu, 60). Anal. Calc. for C<sub>21</sub>H<sub>36</sub>NClGe: C, 61.43, H, 8.84, N, 3.41, Found: C, 61.58, H, 8.91, N, 3.33%.

### 4.4. Synthesis of ArGeC(N<sub>2</sub>)SiMe<sub>3</sub> (**2**)

A solution of lithiotrimethylsilyldiazomethane (7.52 mmol) prepared from a stoichiometric quantity of *n*-butyllithium (8.32 mmol, 5.2 mL, 1.6 M in *n*-hexane) and trimethylsilyldiazomethane (7.52 mmol, 3.76 mL, 2 M in *n*-hexane) was added dropwise at -78 °C to **1** (2.88 g, 7.52 mmol) in THF (15 mL). The brown solution was stirred for 2 h then allowed to warm to room temperature. All volatiles were removed under vacuum and the residue dissolved in pentane. After filtration through Celite, removal of the solvents in vacuum leads to **2** as a yellow solid.

(2.93 g, 6.02 mmol, 80% yield); m.p.: 113 °C (dec.); <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>), δ (ppm): 0.35 (s, 9H, Me<sub>3</sub>Si), 0.84 (d, <sup>3</sup>J<sub>H/H</sub> = 6.7 Hz, 6H,

CH(CH<sub>3</sub>)<sub>2</sub>), 0.90 (d, <sup>3</sup>J<sub>H/H</sub> = 6.7 Hz, 3H, CH(CH<sub>3</sub>)<sub>2</sub>), 1.25 (d, <sup>3</sup>J<sub>H/H</sub> = 6.7 Hz, 3H, CH(CH<sub>3</sub>)<sub>2</sub>), 1.35 (s, 9H, C(CH<sub>3</sub>)<sub>3</sub>), 1.58 (s, 9H, C(CH<sub>3</sub>)<sub>3</sub>), 3.14 (sept, <sup>3</sup>J<sub>H/H</sub> = 6.7 Hz, 1H, CH(CH<sub>3</sub>)<sub>2</sub>), 3.82–3.93 (AB system, <sup>2</sup>J<sub>H/H</sub> = 15.2 Hz, 2H, CH<sub>2</sub>N), 3.87 (sept, <sup>3</sup>J<sub>H/H</sub> = 6.7 Hz, 1H, CH(CH<sub>3</sub>)<sub>2</sub>), 7.15 (d, <sup>4</sup>J<sub>H/H</sub> = 3.2 Hz, 1H, H<sub>5</sub>), 7.54 (d, <sup>4</sup>J<sub>H/H</sub> = 3.2 Hz, 1H, H<sub>5</sub>); <sup>13</sup>C NMR (C<sub>6</sub>D<sub>6</sub>), δ (ppm): –0.28 (CH<sub>3</sub>Si), 18.68 (CH(CH<sub>3</sub>)<sub>2</sub>), 20.58 (CH(CH<sub>3</sub>)<sub>2</sub>), 21.63 (CH(CH<sub>3</sub>)<sub>2</sub>), 23.40 (CH(CH<sub>3</sub>)<sub>2</sub>), 26.82 (CN<sub>2</sub>), 31.37 (C(CH<sub>3</sub>)<sub>3</sub>), 32.11 (C(CH<sub>3</sub>)<sub>3</sub>), 34.50 (C(CH<sub>3</sub>)<sub>3</sub>), 37.37 (C(CH<sub>3</sub>)<sub>3</sub>), 51.80 (CH(CH<sub>3</sub>)<sub>2</sub>), 57.37 (CH(CH<sub>3</sub>)<sub>2</sub>), 60.17 (CH<sub>2</sub>), 118.24 (3-aryl-C), 120.66 (5-aryl-C), 145.98 (2-aryl-C), 149.64 (4-aryl-C), 153.88 (1-aryl-C), 155.60 (6-aryl-C); <sup>29</sup>Si NMR (C<sub>6</sub>D<sub>6</sub>), δ (ppm): –0.25; IR (C<sub>6</sub>D<sub>6</sub>): ν(CN<sub>2</sub>) = 2002.9 cm<sup>–1</sup>; EI-MS (70 eV), *m/z* (%): 489 (M<sup>+</sup>, 20), 446 (M<sup>+</sup>–iPr, 5), 376 (ArGe, 100); UV (pentane) λ<sub>max</sub> (ε): 366 nm (126). Anal. Calc. for C<sub>25</sub>H<sub>45</sub>N<sub>3</sub>GeSi: C, 61.49, H, 9.29, N, 8.60; Found: C, 61.60, H, 9.38, N, 8.49%.

#### 4.5. Reaction of **3** with *t*-BuOH/H<sub>2</sub>O, synthesis of **4**

A solution of **2** (77 mg, 0.16 mmol) in 2 mL of *tert*-butyl alcohol and 2.8 μL of water was photolyzed at room temperature in a quartz Schlenk for 30 min. Then the *tert*-butyl alcohol was eliminated under vacuum and the residue, a waxy material, dissolved in C<sub>6</sub>D<sub>6</sub> was identified to **4**.

(75 mg, 0.136 mmol, 85% yield); <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>), δ (ppm): 0.30 (s, 9H, Me<sub>3</sub>Si), 0.74–0.87 (AB system, <sup>2</sup>J<sub>H/H</sub> = 15.1 Hz, 2H, CH<sub>2</sub>SiMe<sub>3</sub>), 1.05 (d, <sup>3</sup>J<sub>H/H</sub> = 6.7 Hz, 6H, CH(CH<sub>3</sub>)<sub>2</sub>), 1.11 (d, <sup>3</sup>J<sub>H/H</sub> = 6.7 Hz, 6H, CH(CH<sub>3</sub>)<sub>2</sub>), 1.36 (s, 9H, C(CH<sub>3</sub>)<sub>3</sub>), 1.36 (s, 9H, OC(CH<sub>3</sub>)<sub>3</sub>), 1.65 (s, 9H, C(CH<sub>3</sub>)<sub>3</sub>), 3.00 (sept, <sup>3</sup>J<sub>H/H</sub> = 6.7 Hz, 2H, CH(CH<sub>3</sub>)<sub>2</sub>), 3.90–4.48 (AB system, <sup>2</sup>J<sub>H/H</sub> = 15.1 Hz, 2H, CH<sub>2</sub>N), 7.63 (br, 1H, H<sub>3</sub>), 7.65 (br, 1H, H<sub>5</sub>), 7.98 (br s, 1H, OH); <sup>13</sup>C NMR (C<sub>6</sub>D<sub>6</sub>), δ (ppm): 1.01 (CH<sub>3</sub>Si), 13.13 (CH<sub>2</sub>SiMe<sub>3</sub>), 19.98 (CH(CH<sub>3</sub>)<sub>2</sub>), 21.73 (CH(CH<sub>3</sub>)<sub>2</sub>), 31.11 (C(CH<sub>3</sub>)<sub>3</sub>), 32.65 (OC(CH<sub>3</sub>)<sub>3</sub>), 33.33 (C(CH<sub>3</sub>)<sub>3</sub>), 34.66 (C(CH<sub>3</sub>)<sub>3</sub>), 37.13 (C(CH<sub>3</sub>)<sub>3</sub>), 47.37 (CH(CH<sub>3</sub>)<sub>2</sub>), 51.36 (CH<sub>2</sub>NiPr<sub>2</sub>), 73.38 (OC(CH<sub>3</sub>)<sub>3</sub>), 121.96 (3-aryl-C), 128.70 (5-aryl-C), 137.82 (1-aryl-C), 147.00 (2-aryl-C), 150.86 (4-aryl-C), 155.14 (6-aryl-C); <sup>29</sup>Si NMR (C<sub>6</sub>D<sub>6</sub>), δ (ppm): 0.73; EI-MS (70 eV), *m/z* (%): 536 (M–OH, 10), 480 (M–OtBu, 30), 436 (M–OH–NiPr<sub>2</sub>, 100); CI-MS (NH<sub>3</sub>), *m/z* (%): 554 (M+H<sup>+</sup>, 100).

#### 4.6. Reaction of **3** with H<sub>2</sub>O, synthesis of **5**

A solution of **2** (77 mg, 0.16 mmol) in 2 mL of *tert*-butyl alcohol and 5.6 μL of water was photolyzed at room temperature in a quartz Schlenk for 30 min. Then the *tert*-butyl alcohol was eliminated under vacuum leading to a white solid identified to **5**.

(71 mg, 0.142 mmol, 89% yield); m.p.: 127–128 °C; <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>), δ (ppm): 0.35 (s, 9H, Me<sub>3</sub>Si), 0.69 (s, 2H, CH<sub>2</sub>SiMe<sub>3</sub>), 1.01 (d, <sup>3</sup>J<sub>H/H</sub> = 6.7 Hz, 12H, CH(CH<sub>3</sub>)<sub>2</sub>), 1.33 (s, 9H, C(CH<sub>3</sub>)<sub>3</sub>), 1.58 (s, 9H, C(CH<sub>3</sub>)<sub>3</sub>), 3.01 (sept, <sup>3</sup>J<sub>H/H</sub> = 6.7 Hz, 2H, CH(CH<sub>3</sub>)<sub>2</sub>), 4.01 (s, 2H, CH<sub>2</sub>NiPr<sub>2</sub>), 7.44 (d, <sup>4</sup>J<sub>H/H</sub> = 3.1 Hz, 1H, H<sub>3</sub>), 7.64 (d, <sup>4</sup>J<sub>H/H</sub> = 3.1 Hz, 1H, H<sub>5</sub>), 7.98 (br s, 2H, OH); <sup>13</sup>C NMR (C<sub>6</sub>D<sub>6</sub>), δ (ppm): 1.03 (CH<sub>3</sub>Si), 12.44 (CH<sub>2</sub>SiMe<sub>3</sub>), 20.24 (CH(CH<sub>3</sub>)<sub>2</sub>), 30.96 (C(CH<sub>3</sub>)<sub>3</sub>), 33.20 (C(CH<sub>3</sub>)<sub>3</sub>), 34.22 (C(CH<sub>3</sub>)<sub>3</sub>), 37.19 (C(CH<sub>3</sub>)<sub>3</sub>), 46.76 (CH(CH<sub>3</sub>)<sub>2</sub>), 51.49 (CH<sub>2</sub>NiPr<sub>2</sub>), 122.18 (5-aryl-C), 128.70 (3-aryl-C), 137.86 (1-aryl-C), 143.44 (2-aryl-C), 150.38 (4-aryl-C), 156.36 (6-aryl-C); <sup>29</sup>Si NMR (C<sub>6</sub>D<sub>6</sub>), δ (ppm): 1.09; IR (C<sub>6</sub>D<sub>6</sub>): ν (OH) 3617.8 (wide), 3802.1; EI-MS (70 eV), *m/z* (%): 480 [(M–OH), 100]. Anal. Calc. for C<sub>25</sub>H<sub>49</sub>NO<sub>2</sub>GeSi: C, 60.50, H, 9.95, N, 2.82, Found: C, 60.58, H, 10.01, N, 2.75%.

## 5. Crystal structure determination

The structures of two compounds were determined. The selected crystals were mounted on a glass fiber using perfluoropolyether oil and cooled rapidly to 173 K in a stream of cold N<sub>2</sub>.

For all the structures data were collected at low temperature (173 K) on a Bruker-AXS APEX II diffractometer equipped with the Bruker Kryo-Flex cooler device and using a graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). The structures were solved by direct methods [14] and all non-hydrogen atoms were refined anisotropically using the least-squares method on F<sup>2</sup> [15].

**Selected data for the diazomethylgermylene 2:** C<sub>25</sub>H<sub>45</sub>GeN<sub>3</sub>Si, *M* = 488.32, monoclinic, space group Cc, *a* = 11.688(2) Å, *b* = 22.024(4) Å, *c* = 11.1173(19) Å, α = γ = 90°, β = 97.968(3)°, *V* = 2834.2(8) Å<sup>3</sup>, *Z* = 4, crystal size 0.30 × 0.20 × 0.20 mm<sup>3</sup>, 7123 reflections collected (3972 independent, *R*<sub>int</sub> = 0.0227), 310 parameters, *R*<sub>1</sub> [*I* > 2σ(*I*)] = 0.0340, *wR*<sub>2</sub> [all data] = 0.0807, largest difference in peak and hole: 0.308 and –0.267 e Å<sup>–3</sup>.

**Selected data for the gem-germanediol 5:** C<sub>25</sub>H<sub>49</sub>GeNO<sub>2</sub>Si, *M* = 496.33, monoclinic, space group C2/c, *a* = 21.8065(17) Å, *b* = 12.4031(10) Å, *c* = 23.1368(18) Å, α = γ = 90°, β = 113.376(2)°, *V* = 5744.1(8) Å<sup>3</sup>, *Z* = 8, crystal size 0.40 × 0.30 × 0.20 mm<sup>3</sup>, 12,395 reflections collected (4067 independent, *R*<sub>int</sub> = 0.0841), 290 parameters, *R*<sub>1</sub> [*I* > 2σ(*I*)] = 0.0453, *wR*<sub>2</sub> [all data] = 0.0773, largest difference in peak and hole: 0.329 and –0.287 e Å<sup>–3</sup>.

## Appendix A. Supplementary data

CCDC 713960 and 713961 contain the supplementary crystallographic data for **2** and **5**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif). Supplementary data associated with this article (for **1**) can be found, in the online version, at doi:10.1016/j.jorganchem.2009.03.005.

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