

# Bis(trimesitylgermylcarbodiimido)germylene, trimesitylgermylcyanamide and trimesitylgermylcarbodiimide

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## Abstract

Bis(trimesitylgermylcarbodiimido)germylene (**1**), isolated as a white precipitate from the reaction of lithium trimesitylgermylcyanamide with dichloro-germylene, is stable at room temperature in the absence of water and oxygen. The germylene structure is preserved in the reaction with 3,5-di-*t*-butylcatechol, while subsequent addition to 3,5-di-*t*-butylorthoquinone gave the corresponding spirogermane. Thermal decomposition of **1** occurs around 50°C leading to bis(trimesitylgermyl)carbodiimide and polycarbodiimidogermylene. Hydrolysis of **1** gave the corresponding monogermylated derivative of cyanamide (**3**) in two isomeric forms: trimesitylgermylcyanamide (**3a**) and trimesitylgermylcarbodiimide (**3b**), in equilibrium in solution. Isomer **3b** is the first compound to precipitate from a benzene solution. Its structure was established by X-ray diffraction. Compound **3** decomposes on heating to form dicyanamide and bis(trimesitylgermyl)carbodiimide. © 2000 Elsevier Science S.A. All rights reserved.

**Keywords:** Stable germylene; Bis(trimesitylgermylcarbodiimido)germylene; Polycarbodiimido-germylene; Trimesitylgermylcyanamide; Trimesitylgermylcarbodiimide; Bis(trimesitylgermyl)-carbodiimide

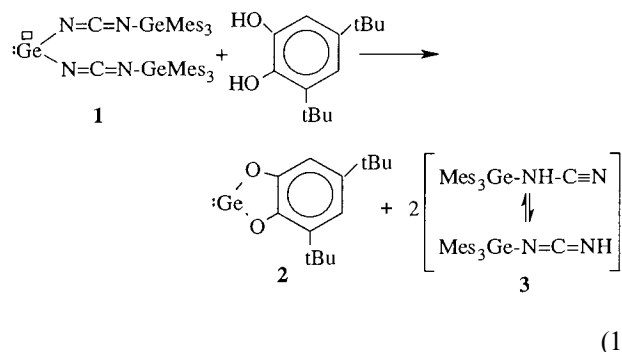
## 1. Introduction

Following our recent studies of germylcarbodiimides and cyanamides of Ge<sub>IV</sub> [1,2], we have attempted to isolate a germylene (Ge<sub>II</sub>) with carbodiimide substituents. Our results on bis(trimesitylgermylcarbodiimido)germylene and its hydrolysis products, trimesitylgermylcyanamide and trimesitylgermylcarbodiimide, are presented here.

## 2. Results and discussion

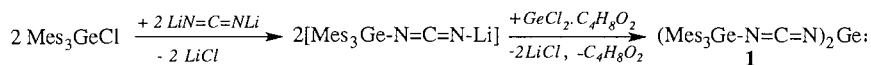
In order to make a stable germylene, which usually requires bulky substituents on germanium and delocalization of a lone pair into the vacant 4d orbitals of the metal [3–5], we used trimesitylgermyl cyanamide lithium and made it react with dichloro-germylene.dioxane [6] at low temperature (Scheme 1).

The germylene formulation of **1** was confirmed by the stoichiometric addition of 3,5-di-*t*-butylcatechol, which gave the corresponding previously known [7] 2-germylene(6,8-di-*t*-butyl)-4,5-benzo-1,3-dioxolane **2** (Eq. (1)), with elimination of trimesitylgermylcyanamide **3**.

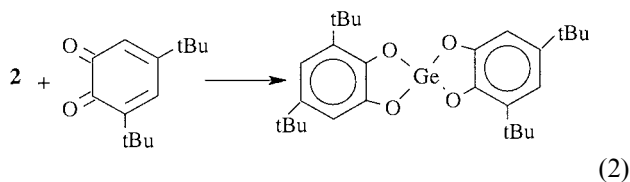


Evidence of the germylene structure of **2**, and therefore of **1**, was obtained by further addition to 3,5-di-*t*-butylorthoquinone, leading to the expected spirogermane [7] (Eq. (2)).

\* Corresponding author.

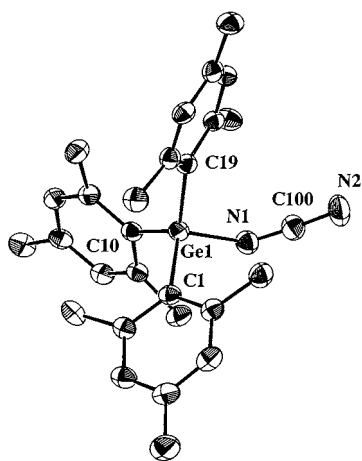
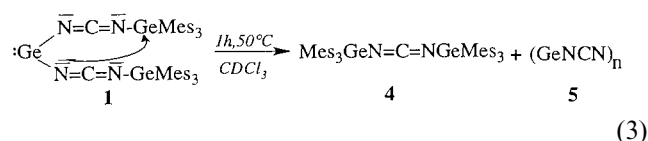


Scheme 1.



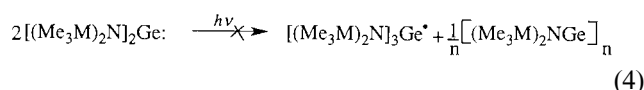
Compound **1** was also characterized spectroscopically. It shows in its infrared spectrum the lowest carbodiimide absorption ( $2088 \text{ cm}^{-1}$ ) within the series of germanium compounds described here, a fact which may be diagnostic of a conjugated compound. This assumption is further supported by the observation that germylene **1** is a poor nucleophile. It did not react with dimethylbutadiene or methyl iodide as do electrophilic germylenes [3,8]. The sharp singlets in its  $^1\text{H-NMR}$  spectrum favor a monomeric structure. Its mass spectrum (DCI- $\text{CH}_4$ ) showed the characteristic molecular ion ( $M+1$ : 1013). Unfortunately, we were unable to obtain single crystals of **1** for an X-ray analysis.

Thermal decomposition of **1** can be followed by  $^1\text{H-NMR}$  by the disappearance of its characteristic signals in  $\text{CDCl}_3$  solution. The decomposition was complete after 4 h at  $50^\circ\text{C}$ , leading to bis(trimesitylgermyl)carbodiimide (**4**) [2] and a white precipitate of polycarbodiimido-germylene (**5**) [9b], probably formed by intra- or intermolecular elimination reactions (Eq. (3)).

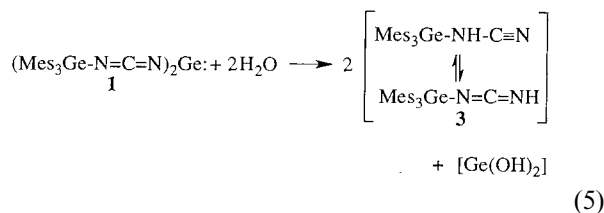
Fig. 1. Molecular structure of **3b** in the solid state.

Compound **5** has been identified by comparison with an authentic sample prepared from  $\text{GeCl}_2 \cdot \text{C}_4\text{H}_8\text{O}_2$  and lithium cyanamide. It shows the characteristic infrared absorption at  $2105 \text{ cm}^{-1}$  of that polymer [9].

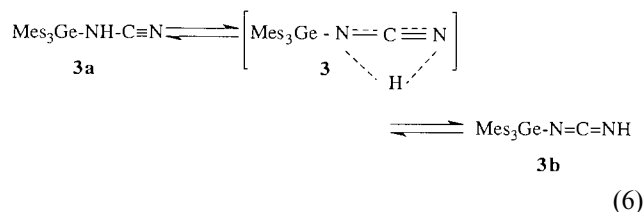
Unlike Lappert's aminogermynes [10,11], **1** appears to be stable in visible light. We did not observe the septet expected for the triaminogermyl-centered radical (Eq. (4)) in its ESR spectrum, upon warming the mixture with or without irradiation.



Hydrolysis of **1** led quantitatively to the monogermyle derivative of cyanamide (Eq. (5)). Note that trimesitylgermylcyanamide was previously characterized spectroscopically in solution, in the presence of nitromethane and in a mixture with trimesitylgermylchloride with an excess of cyanamide, but not isolated [2].



The white crystals of the monogermyle compound **3** were studied by  $^1\text{H}$ -,  $^{13}\text{C}$ -NMR and IR spectroscopy. While the IR spectra of the crystals showed only the  $\text{N}=\text{C}=\text{N}$  absorption at  $2122 \text{ cm}^{-1}$ , the chloroform solutions displayed two IR absorptions at  $2198 \text{ cm}^{-1}$  ( $\nu_{\text{C}=\text{N}}$ ) and  $2149 \text{ cm}^{-1}$  ( $\nu_{\text{N}=\text{C}=\text{N}}$ ). Addition of nitromethane to the solution led to an increase in the intensity of the  $\nu_{\text{C}=\text{N}}$  absorption, suggesting an equilibrium between the two monogermyle forms in solution (Eq. (6)).



The fact that nitromethane favors the cyanamide form **3a** is probably due to the complexation of that solvent as a nucleophile to germanium leading to a more nucleophilic  $\alpha$ -nitrogen atom, therefore more apt to accept the proton.

Similar phenomena have been observed in the NMR spectra. In the  $^{13}\text{C}$ -NMR spectra, besides the two qua-



### 3.1. Preparation of **1**

To  $\text{H}_2\text{NCN}$  (0.07 g, 1.72 mmol) in 4 ml of THF at  $-70^\circ\text{C}$  was added dropwise with stirring a solution of *t*-BuLi in pentane (3.44 mmol, 2.02 ml, 1.7 M). After 30 min at r.t. the mixture was cooled again to  $-60^\circ\text{C}$  and  $\text{Mes}_3\text{GeCl}$  (0.80 g, 1.72 mmol) in 6 ml of THF was added dropwise with stirring. After 1 h at  $-60^\circ\text{C}$ ,  $\text{GeCl}_2$ .dioxane (0.19 g, 0.86 mmol) in 2 ml of THF was added dropwise with stirring. The mixture was kept at  $-30^\circ\text{C}$  for 16 h. THF was then replaced by benzene and lithium chloride centrifuged. Evaporation of the solvents under vacuum afforded 0.33 g of a white powder of **1** (yield 72%) which was unstable in air.

M.p.:  $108^\circ\text{C}$  with decomposition.  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ ):  $\delta_{\text{ppm}}$ , 2.20 (s, 54H,  $\text{CH}_3$ ); 6.72 (s, 12H,  $\text{C}_6\text{H}_2$ ).  $^{13}\text{C-NMR}$  ( $\text{CDCl}_3$ ):  $\delta_{\text{ppm}}$ , 21.04 (*p*- $\text{CH}_3$ ); 23.97 (*o*- $\text{CH}_3$ ); 143.64 ( $\text{C}_2$ ); 128.92 ( $\text{C}_3$ ); 138.60 ( $\text{C}_4$ ); 136.00; 135.68 ( $\text{C}_1$ ; NCN); ( $\text{C}_6\text{D}_6$ )  $\delta_{\text{ppm}}$ , 21.02 (*p*- $\text{CH}_3$ ); 24.21 (*o*- $\text{CH}_3$ ); 143.84 ( $\text{C}_2$ ); 130.17( $\text{C}_3$ ); 139.50( $\text{C}_4$ ). IR ( $\text{CDCl}_3$ ): ( $\nu_{\text{as}} \text{NCN}$ ):  $2088 \text{ cm}^{-1}$ . MS (DCI- $\text{CH}_4$ ), *m/z*, %): 1013, 2% [ $\text{M} + 1$ ].

### 3.2. Reaction of 3,5-di-*t*-butylcatechol with **1**, followed by reaction with 3,5-di-*t*-butylorthoquinone

To **1** (0.34 g, 0.34 mmol) in 3 ml of THF was added dropwise with stirring at r.t. a solution of 3,5-di-*t*-butylcatechol (0.08 g, 0.34 mmol) in 2 ml of THF. After 4 h at r.t., THF was evaporated under vacuum yielding a white sticky residue consisting of **3** (69%) and 2-germylene(6,8-di-*t*-butyl)-4,5-benzo-1,3-dioxolane **2** (31%) characterized by comparison with an authentic sample [7]. Addition of an equivalent of 3,5-di-*t*-butylorthoquinone gave the expected spirogermane [7] identified by  $^1\text{H-NMR}$ .

### 3.3. Attempts at addition reactions to **1**

To **1** (0.33 g, 0.32 mmol) in 3 ml of THF was added with stirring at r.t. dimethylbutadiene (0.03 g, 0.32 mmol). After 5 h of reaction at r.t. only thermal decomposition products of **1** were recovered. The same result was observed with methyl iodide.

### 3.4. Thermal decomposition of **1**

A solution of **1** (0.05 g, 0.05 mmol) in 0.5 ml of  $\text{CDCl}_3$  was heated to  $50^\circ\text{C}$  for 1 h. The decomposition was followed by  $^1\text{H-NMR}$ , showing the formation of **4**. A white precipitate not soluble in usual organic solvents was identified (by its infrared spectrum:  $\nu_{\text{N}=\text{C}=\text{N}}$ :  $2105 \text{ cm}^{-1}$ ) as  $(\text{GeNCN})_n$  **5** [9], but it was too sensitive to hydrolysis for microanalysis.

### 3.5. Photochemical stability of **1**

A similar sample of **1** dissolved in 0.3 ml of THF and 0.3 ml of toluene was placed in a quartz tube at  $-60^\circ\text{C}$  in the ESR cavity. The sample was irradiated and warmed progressively. The expected septet was not observed, indicating that **1** is stable under these conditions.

### 3.6. Hydrolysis of **1** to yield **3**

At r.t. 0.3 g of **1** in 4 ml of benzene left in an open flask afforded colorless crystals, which slowly deposited on the vessel walls near the liquid surface. 0.21 g of these crystals were obtained and identified as **3b** (yield 75%) by X-ray analysis. M.p.:  $127\text{--}129^\circ\text{C}$ . IR (KBr): ( $\nu_{\text{as}} \text{NCN}$ ):  $2122 \text{ cm}^{-1}$ . Anal. Calc. for  $\text{C}_{28}\text{H}_{34}\text{GeN}_2$ , C, 71.37; H, 7.27; N, 5.95. Found: C, 71.45; H, 6.99; N, 5.54%.

### 3.7. Tautomeric equilibrium **3a/3b** as followed by IR and $^{13}\text{C-NMR}$ studies

A reference solution of **3** was prepared by dissolving **3** (0.02 g, 0.04 mmol) in 1.5 ml of chloroform. To 0.5 ml of this solution was added 0.1 ml of nitromethane. The reference solution and the solution with nitromethane were analyzed by IR spectroscopy. The presence of nitromethane increased the intensity of the  $\nu_{\text{C}=\text{N}}$  absorption. IR ( $\text{CDCl}_3$ ): ( $\nu_{\text{as}} \text{CN}$ ):  $2198 \text{ cm}^{-1}$ ; ( $\nu \text{N-H}$ ):  $3388 \text{ cm}^{-1}$ ; ( $\nu_{\text{as}} \text{NCN}$ ):  $2149 \text{ cm}^{-1}$ .  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ , 80 MHz):  $\delta_{\text{ppm}}$ , 2.21 (s, 18H, *o*- $\text{CH}_3$ ); 2.25 (s, 9H, *p*- $\text{CH}_3$ ); 6.82 (s, 6H,  $\text{C}_6\text{H}_2$ ).

For  $^{13}\text{C-NMR}$  analysis, the reference solution was prepared in 1.5 ml of  $\text{CDCl}_3$ . To 1.5 ml of this solution was added 0.05 ml of  $\text{CH}_3\text{NO}_2$ . In the  $^{13}\text{C-NMR}$  spectrum, there were two sets of carbon signals, one of which was enhanced by the presence of  $\text{CH}_3\text{NO}_2$  and attributed to the cyanamide form **3a**:  $\delta_{\text{ppm}}$ , 21.09 (*p*- $\text{CH}_3$ ); 23.87 (*o*- $\text{CH}_3$ ); 134.29 ( $\text{C}_1$ ); 143.18 ( $\text{C}_2$ ); 129.96( $\text{C}_3$ ); 139.88 ( $\text{C}_4$ ); 122.55 ( $\text{C}=\text{N}$ ). The other carbons signals were attributed to carbodiimide **3b**:  $\delta_{\text{ppm}}$ , 21.09 (*p*- $\text{CH}_3$ ); 24.08 (*o*- $\text{CH}_3$ ); 134.29 ( $\text{C}_1$ ); 143.29 ( $\text{C}_2$ ); 129.67 ( $\text{C}_3$ ); 139.35 ( $\text{C}_4$ ); 135.21 ( $\text{N}=\text{C}=\text{N}$ ). MS (EI, *m/z*, %): 472, 5% [ $\text{M}^+$ ]; 457, 6% [ $\text{M}^+ - \text{NH}$ ]; 431, 100% [ $\text{M}^+ - \text{NH} - \text{CN}$ ]; 352, 45% [ $\text{M}^+ - \text{MesH}$ ].

### 3.8. X-ray analysis of **3b**

Crystal data for **3b**:  $\text{C}_{31}\text{H}_{36}\text{GeN}_2$ ,  $M = 509.21$ , triclinic,  $P\bar{1}$ ,  $a = 8.957(1) \text{ \AA}$ ,  $b = 16.303(2) \text{ \AA}$ ,  $c = 18.505(2) \text{ \AA}$ ,  $\alpha = 80.07(1)^\circ$ ,  $\beta = 83.89(1)^\circ$ ,  $\gamma = 89.39(1)^\circ$ ,  $V = 2646.5(5) \text{ \AA}^3$ ,  $Z = 4$ ,  $\rho_c = 1.278 \text{ Mg m}^{-3}$ ,  $F(000) = 1072$ ,  $\lambda = 0.71073 \text{ \AA}$ ,  $T = 173(2) \text{ K}$ ,  $\mu(\text{Mo-K}\alpha) = 1.179 \text{ mm}^{-1}$ , crystal size  $0.6 \times 0.5 \times 0.1 \text{ mm}$ ,  $2.29^\circ < \theta < 22.72^\circ$ , 18 536 reflections (6758 independent,  $R_{\text{int}} =$

0.1145) were collected at low temperature using an oil-coated shock-cooled crystal [18] on a STOE-IPDS diffractometer. The structure was solved by direct methods (SHELXS-97) [19] and 628 parameters using 172 restraints were refined using the least-squares method on  $F^2$  [20]. The largest electron density residue was:  $1.071 \text{ e } \text{Å}^{-3}$ ,  $R_1$  (for  $F > 2\sigma(F)$ ) = 0.070 and  $wR_2 = 0.200$  (all data) with  $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$  and  $wR_2 = (\Sigma w(F_o^2 - F_c^2)^2 / \Sigma w(F_o^2)^{0.5})$ . It was not possible to locate the hydrogen atoms in the N–C–N unit.

### 3.9. Preparation of **4** from **3**

To a mixture of **3** (0.30 g, 0.63 mmol) and  $\text{Me}_3\text{GeCl}$  (0.29 g, 0.63 mmol) in 4 ml of THF,  $\text{Et}_3\text{N}$  (0.07 g, 0.63 mmol) was added with stirring at r.t. After 3 h, THF was replaced by 4 ml of benzene and  $\text{Et}_3\text{N}\cdot\text{HCl}$  was separated by centrifugation. The remaining solution was evaporated under vacuum and afforded 0.41 g of a white powder of **4** [2]. Yield 64%.

### 3.10. Thermal stability of **3**

A solution of **3** (0.20 g, 0.42 mmol) in 0.8 ml of  $\text{CDCl}_3$  was warmed to  $80^\circ\text{C}$  for 18 h. The reaction was followed by  $^1\text{H-NMR}$  until complete decomposition of **3** afforded 0.006 g of a white precipitate of dicyanamide (yield: 67%; m.p.:  $210^\circ\text{C}$ ). The remaining solution after evaporation of the solvents under vacuum led to 0.15 g of **4** (yield: 78%) [2].

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