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Bis(trimesitylgermylcarbodiimido)germylene, trimesitylgermylcyanamide and trimesitylgermylcarbodiimide

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Received 14 May 1999; accepted 23 September 1999

Abstract

Bis(trimesitylgermylcarbodiimido)germylene (**1**), isolated as a white precipitate from the reaction of lithium trimesitylgermylcyanamide with dichlorogermylene, 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

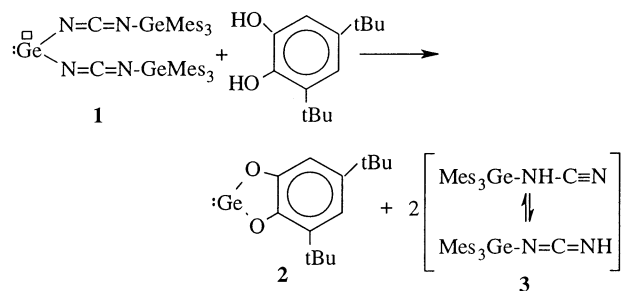
1. Introduction

Following our recent studies of germylcarbodiimides and cyanamides of Ge_{IV} [1,2], we have attempted to isolate a germylene (Ge_{II}) 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 dichlorogermylene.dioxane [6] at low temperature (Scheme 1).

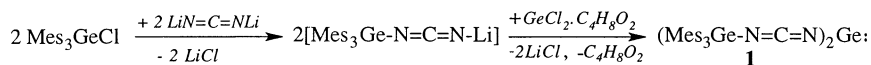
The germylene formulation of **1** was confirmed by the stoichiometric addition of 3,5-di-*t*-butylcatechol, which gave the corresponding previously known [7] 2-germylene(6,8-di-*t*-butyl)-4,5-benzo-1,3-dioxolane **2** (Eq. (1)), with elimination of trimesitylgermylcyanamide **3**.



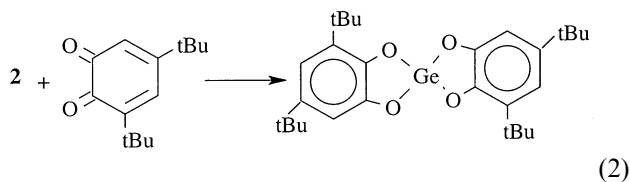
(1)

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)).

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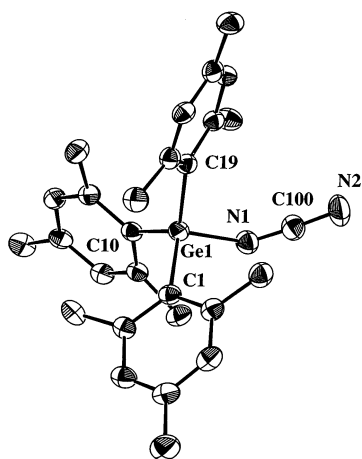
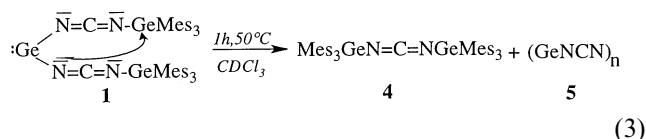


Scheme 1.



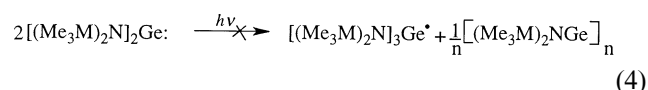
Compound **1** was also characterized spectroscopically. It shows in its infrared spectrum the lowest carbodiimide absorption (2088 cm^{-1}) within the series of germanium compounds described here, a fact which may be diagnostic of a conjugated compound. This assumption is further supported by the observation 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-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 CDCl_3 solution. The decomposition was complete after 4 h at 50°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)).

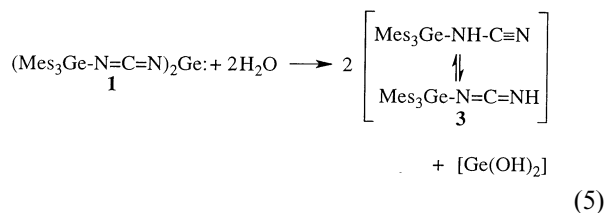
Fig. 1. Molecular structure of **3b** in the solid state.

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 cm^{-1} of that polymer [9].

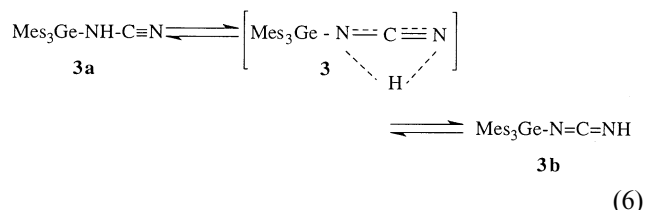
Unlike Lappert's aminogermynes [10,11], **1** appears to be stable in visible light. We did not observe the septet expected for the triaminogermyl-centered radical (Eq. (4)) in its ESR spectrum, upon warming the mixture with or without irradiation.



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

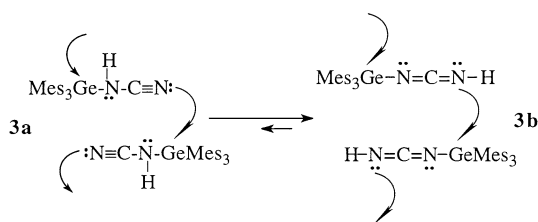


The fact that nitromethane favors the cyanamide form **3a** is probably due to the complexation of that solvent as a nucleophile to germanium leading to a more nucleophilic α -nitrogen atom, therefore more apt to accept the proton.

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

Table 1
Selected bond lengths (Å) and angles (°) for **3b**

<i>Bond lengths</i>	
Ge1–N1	1.866(5)
N1–C100	1.236(9)
C100–N2	1.213(9)
Ge1–C1	1.981(5)
Ge1–C10	1.963(6)
Ge1–C19	1.959(5)
<i>Bond angles</i>	
N1–C100–N2	171.3(8)
Ge1–N1–C100	134.4(5)
C1–Ge1–N1	102.0(2)
C10–Ge1–N1	102.0(2)
C19–Ge1–N1	104.8(2)



Scheme 2.

ternary carbon atoms $C\equiv N$ and $N=C=N$, there are two sets of carbon signals, one of which is enhanced by the presence of nitromethane, confirming the equilibrium in Eq. (6).

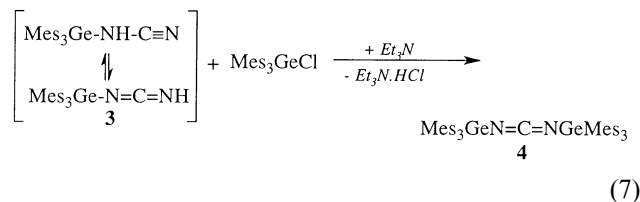
The first isomer to precipitate from a benzene solution was **3b**. The unit cell of this crystals analyzed by X-ray diffraction showed two moles of **3b** for one mole of benzene. The structure of **3b** (Fig. 1) is the first example of a monometallated cyanamide derivative of a Group 14 element. There is no intermolecular interaction observed in the solid state. The first neighboring atoms are in the range of 3 Å. The molecule is represented in Fig. 1, and selected bond lengths and angles are given in Table 1.

Note that the similarity in bond lengths of C–N1 and C–N2 in the crystal (C100–N1: 1.23 Å, C100–N2: 1.21 Å) is in agreement with the molecular model of isomer **3b** calculated for the more stable carbodiimide conformer (E : 26.75 kcal mol^{−1}) (C100–N1 = C100–N2 = 1.26 Å), while the same calculation for the cyanamide conformer **3a** (E : 28.89 kcal mol^{−1}) gives different values (C100–N1: 1.40 Å ≠ C100–N2: 1.13 Å) (Program Insight I discover, Biosym/MSI, force field ESFF). A similarity in bond lengths has also been reported for bis(trimesitylgermyl)carbodiimide (1.20 and 1.19 Å, respectively) [2].

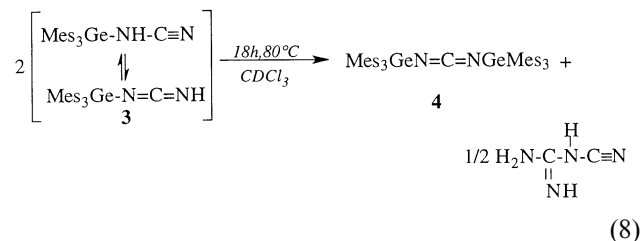
Isomer **3b** is monomeric in the crystal. For the solution state we have no arguments in favor of (or against) an intermolecular coordination for **3**, such as the one observed for tributylcyanamide [12,13]. A similar mech-

anism involving pentacoordinate germanium (Scheme 2) could be the first step in the equilibrium of Eq. (6).

Compound **3** is stable at room temperature (r.t.). With trimesitylgermylchloride in the presence of triethylamine, it yields the expected bis(trimesitylgermyl)carbodiimide **4** [2] (Eq. (7)).



However compound **3** is not thermally stable. On heating it, bis(trimesitylgermylcarbodiimide **4** is formed with elimination of dicyanamide (Eq. (8)). The reaction is similar to the intermolecular deamination usually observed for less bulky germyl derivatives of secondary amines [3,11,15].



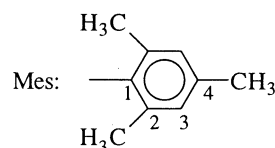
Note that a similar decomposition was observed for stannyl cyanamide [14,16], and that, although often postulated, silicon cyanamides have never been isolated [17].

3. Experimental

All reactions were carried out under nitrogen or argon and with dry solvents.

NMR spectra were recorded on Bruker AC 80 (¹H) and AC 200 (¹³C; in the sequence J_{mod}) spectrometers ($\delta_{\text{ppm}}/\text{TMS}$); IR spectra on a Perkin–Elmer 1600 FTIR spectrometer; mass spectra on a Hewlett–Packard HP 5989 in the electron impact mode (70 eV) or on a Rybermag R10-10 spectrometer operating in the electron impact mode or by chemical desorption (DCI–CH₄). Melting points (m.p.) were measured on a Leitz microscope.

ESR experiments were performed on a Bruker ER 200 with Frequencymer E.I.P. ¹³C numbering for aromatic carbons in mesityl groups was:



3.1. Preparation of **1**

To H_2NCN (0.07 g, 1.72 mmol) in 4 ml of THF at -70°C was added dropwise with stirring a solution of $t\text{-BuLi}$ in pentane (3.44 mmol, 2.02 ml, 1.7 M). After 30 min at r.t. the mixture was cooled again to -60°C and Me_3GeCl (0.80 g, 1.72 mmol) in 6 ml of THF was added dropwise with stirring. After 1 h at -60°C , $\text{GeCl}_2\cdot\text{dioxane}$ (0.19 g, 0.86 mmol) in 2 ml of THF was added dropwise with stirring. The mixture was kept at -30°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°C with decomposition. $^1\text{H-NMR}$ (CDCl_3): δ_{ppm} , 2.20 (s, 54H, CH_3); 6.72 (s, 12H, C_6H_2). $^{13}\text{C-NMR}$ (CDCl_3): δ_{ppm} , 21.04 ($p\text{-CH}_3$); 23.97 ($o\text{-CH}_3$); 143.64 (C_2); 128.92 (C_3); 138.60 (C_4); 136.00; 135.68 (C_1 ; NCN); (C_6D_6) δ_{ppm} , 21.02 ($p\text{-CH}_3$); 24.21 ($o\text{-CH}_3$); 143.84 (C_2); 130.17 (C_3); 139.50 (C_4). IR (CDCl_3): ($\nu_{\text{as}} \text{NCN}$): 2088 cm^{-1} . MS (DCI-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 CDCl_3 was heated to 50°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 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°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 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 (CDCl_3): ($\nu_{\text{as}} \text{CN}$): 2198 cm^{-1} ; ($\nu \text{N-H}$): 3388 cm^{-1} ; ($\nu_{\text{as}} \text{NCN}$): 2149 cm^{-1} . $^1\text{H-NMR}$ (CDCl_3 , 80 MHz): δ_{ppm} , 2.21 (s, 18H, $o\text{-CH}_3$); 2.25 (s, 9H, $p\text{-CH}_3$); 6.82 (s, 6H, C_6H_2).

For $^{13}\text{C-NMR}$ analysis, the reference solution was prepared in 1.5 ml of CDCl_3 . To 1.5 ml of this solution was added 0.05 ml of CH_3NO_2 . In the $^{13}\text{C-NMR}$ spectrum, there were two sets of carbon signals, one of which was enhanced by the presence of CH_3NO_2 and attributed to the cyanamide form **3a**: δ_{ppm} , 21.09 ($p\text{-CH}_3$); 23.87 ($o\text{-CH}_3$); 134.29 (C_1); 143.18 (C_2); 129.96 (C_3); 139.88 (C_4); 122.55 ($\text{C}\equiv\text{N}$). The other carbons signals were attributed to carbodiimide **3b**: δ_{ppm} , 21.09 ($p\text{-CH}_3$); 24.08 ($o\text{-CH}_3$); 134.29 (C_1); 143.29 (C_2); 129.67 (C_3); 139.35 (C_4); 135.21 ($\text{N}=\text{C}=\text{N}$). MS (EI, m/z , %): 472, 5% [$\text{M}^+\cdot$]; 457, 6% [M^+-NH]; 431, 100% [$\text{M}^+-\text{NH-CN}$]; 352, 45% [M^+-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: $1.071 \text{ e } \text{\AA}^{-3}$, 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 $wR_2 = (\Sigma w(F_o^2 - F_c^2)^2 / \Sigma w(F_o^2)^2)^{0.5}$. 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 Me_3GeCl (0.29 g, 0.63 mmol) in 4 ml of THF, Et_3N (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 CDCl_3 was warmed to 80°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°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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