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Synthesis and Structure of Oligomeric Dimesitylgermyl-Substituted Carbodiimides; Characterization of Higher Oligomers

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New cyclic oligomers of dimesitylgermylene carbodiimides $(\mathrm{Mes_2GeNCN})_n$ ($n = 3$ (**1**) and 4 (**2**)) were synthesized by reactions of dimesityldichlorogermane with either cyanamide in the presence of triethylamine or lithium cyanamide. The reactions always gave **1**, the trimer of the hypothetical $(\mathrm{Mes_2Ge{=}N{-}CN})$, as the major compound. Higher oligomers **3** (n up to 20−30) also can be isolated, depending on the reaction conditions. In THF solution at room temperature, **2** and **3** slowly isomerize to **1**, which seems to be the most stable compound. X-ray analysis of trimer **1** and tetramer **2** shows unstrained tetrahedral germanium atoms and linear diimine linkers.

Introduction

Although dimeric $-[\mathrm{Me_2GeN{=}C{=}N}]-_2$ was postulated once[1] in an exchange reaction between $\mathrm{Me_2GeF_2}$ and bis(trimethylsilyl)carbodiimide, such cyclic oligomers have never been isolated nor characterized. Silicon analogues have been reported only recently;[2−4] the tetramer $-(\mathrm{Me_2Si{-}N{=}C{=}N})-_4$ has been thoroughly studied. It is composed of planar 16-membered rings with four $\mathrm{SiMe_2}$ groups connecting the four NCN groups.[4] In view of our interest in the synthesis of new organometallic polymers and since oligomeric metal carbodiimides are precursors for the pyrolytic synthesis of M/C/N ceramics,[2,3] we attempted to synthesize such compounds and present our results within the germanium series here.

Results and Discussion

As mesityl groups on germanium tend to stabilize small molecules thought to be unstable or known only as transient species,[6,7] we began our study with mesityl substituents on germanium in the hope of being able to characterize the hypothetical monomer $[\mathrm{Mes_2Ge{=}N{-}C{\equiv}N}]$.

A starting material for the formation of a germanium−nitrogen double bond is the corresponding chlorogermylamine, which, depending on the nature of R, can be unstable, decomposing as shown, Scheme 1.[6,8−10]

When cyanamide was used instead of a primary amine in an equimolar ratio in a reaction with dimesityldichlorogermane in the presence of $\mathrm{Et_3N}$, the corresponding monochlorogermane could not be isolated and the formation of any $>$N−H compounds was not observed, in contrast to what was previously observed in the case of trimesitylgermyl compounds.[11] Instead, the bis(dimesitylchlorogermyl)carbodiimide (Scheme 2, *ii*) could be characterized in a mixture with the final oligomeric compounds and some starting material. When two or more equivalents of triethylamine were used (Scheme 2, *iii* and *iv*), the only final product in THF solution (or in the presence of an excess of cyanamide) (Scheme 2, *vi*) was the cyclic trimer **1**. Thus, although **1** can be formed, in principle, through the polymerization of the monomeric hypothetical $[\mathrm{Mes_2Ge{=}N{-}CN}]$ (Scheme 2, *v*), it certainly is obtained through intermolecular elimination between the dichlorogermane and the cyanamide (Scheme 2, *iv*), as previously observed in the case of cyclogermazane formation.[12]

It was not possible to isolate a pure sample of bis(dimesitylchlorogermyl)carbodiimide from the reaction

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(1) Drake, J. E.; Glavincevski, B. M.; Henderson, H. E. *Synth. React. Inorg., Met. Org. Chem.* **1978**, *8*, 7.

(2) Seyferth, D.; Strohmann, C.; Dando, N. R.; Perrota, A. J.; Gardner, J. P. *Mater. Res. Soc. Sympos. Proc.* **1994**, *327*, 191.

(3) Kienzle, A.; Obermeyer, A.; Riedel, R.; Aldinger, F.; Simon, A. *Chem. Ber.* **1993**, *126*, 2569.

(4) Obermeyer, A.; Kienzle, A.; Weidlein, J.; Riedel, R.; Simon, A. *Z. Anorg. Allg. Chem.* **1994**, *620*, 1357.

(5) Gordetsov, A. S.; Kozyukov, V. P.; Vostokov, I. A.; Sheludyakova, S. V.; Dergunov, Yu. I.; Mironov, V. F. *Russ. Chem. Rev.* **1982**, *51*, 485; *Usp. Khim.* **1982**, *51*, 848.

(6) Rivière, P.; Rivière-Baudet, M.; Satgé, J. *Comprehensive Organometallic Chemistry*; Wilkinson, G., Gordon, F., Stone, F. G. A., Abel, E. W., Eds.; Pergamon: New York, 1982; Vol. 2, Chapter 10; *Ibid.* Abel, E. W., Gordon, F., Stone, F. G. A., Wilkinson, G., Davies, A., Eds.; Pergamon: New York, 1995; Vol. 2, Chapter 5.

(7) Escudié, J.; Couret, C.; Ranaivonjatovo H.; Satgé, J. *Coord. Chem. Rev.* **1994**, *130*, 427.

(8) Rivière-Baudet, M. *Main Group Met. Chem.* **1995**, *18*, 353.

(9) Rivière-Baudet, M.; Morère, A.; Khallaayoun, A.; Satgé, J. *Main Group Met. Chem.* **1992**, *15*, 255.

(10) Rivière-Baudet, M.; Khallaayoun, A.; Satgé, J.; Ahra, M. *Synth. React. Inorg. Met.—Org. Chem.* **1992**, *22*, 683.

(11) Dahrouch, M.; Rivière-Baudet, M.; Bertrand, G.; Gornitzka, H. *J. Organomet. Chem.*, submitted for publication.

(12) Rivière-Baudet, M.; El Baz, F.; Satgé, J.; Khallaayoun, A.; Ahra, M. *Phosphorus, Sulfur Silicon Relat. Elem.* **1996**, *112*, 203.

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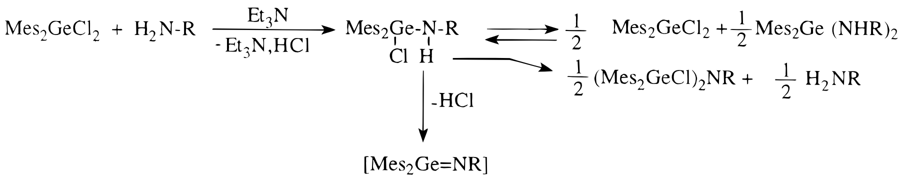
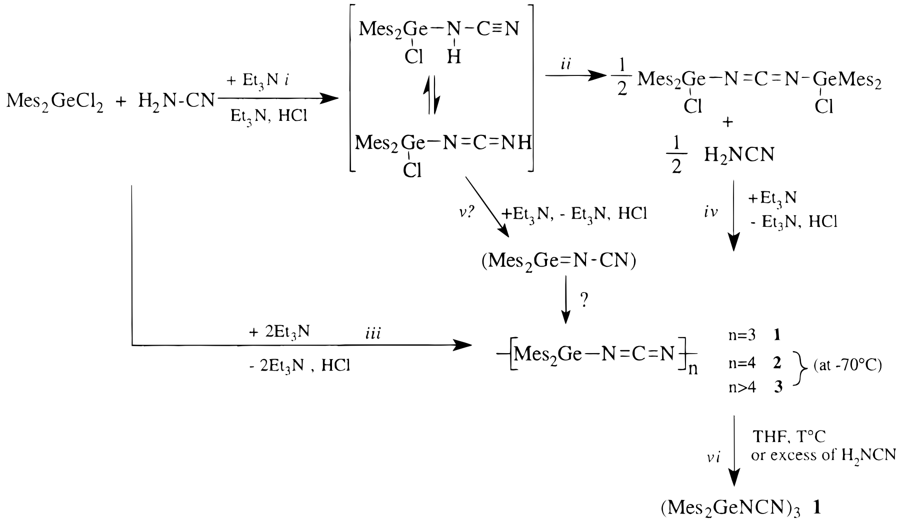
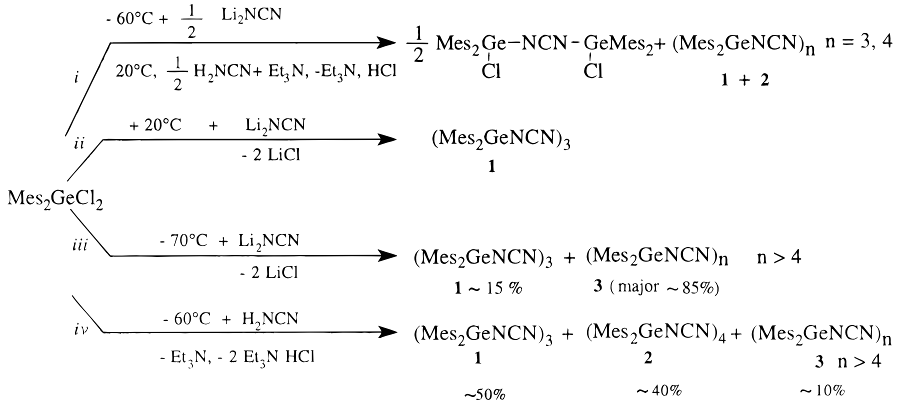
Scheme 1



Scheme 2



Scheme 3



of dimesityldichlorogermane with either cyanamide or lithium cyanamide in a 2:1 ratio (Scheme 3, *i*). Even at low temperature, the reaction always afforded at least small amounts of **1** (Scheme 3, *i*) in addition to the expected bis(dimesithylchlorogermyl)carbodiimide. This (dichlorogermyl)carbodiimide, as soon as formed, probably reacts with the cyanamide reagent in the reaction mixture, as expected from Scheme 2, *iv*.

A 1:1 ratio of reagents at room temperature led to **1** (Scheme 3, *ii*), while at low temperature we were able to characterize two higher cyclooligomers, the tetramer **2**, and a higher oligomer **3** (Scheme 3, *iii* and *iv*). The formation of **3** is favored by dilution in THF. Formation of **2** and **3** is disfavored in the presence of an excess of cyanamide, which probably induces a protic cleavage of Ge−N bonds of higher polymers to give the more stable trimer (Scheme 2, *vi*). NMR analysis of **3** showed only one type of mesityl signal, with small amounts of **1** and **2** contaminants. Compounds **1**, **2**, and **3** were easily identified by ^{1}H NMR (Figure 1). Gel permeation chromathography (GPC) experiments were performed on **3** with toluene or tetrahydrofuran (THF) as the eluant (see Figure 2). The chromatogram obtained in toluene shows a small fraction of **1**, **2**, and a compound of higher mass identified to $n = 5$ by reference to the calibration curve obtained from pure samples of **1**, **2**, and $Mes_3GeN{=}C{=}NGeMes_3$[11] (accuracy of determination about $M = 50-100$). We also observed a broad peak due to species of higher molecular weight ($n > 5$) up to 10 000 $g \cdot mol^{-1}$ (relative to polystyrene standards). The number-average molecular weight (M_n) and weight-average molecular weight (M_w) were, respectively, around 5000 $g \cdot mol^{-1}$ and 7000 $g \cdot mol^{-1}$ (versus polystyrene), with a low dispersity (I) of 1.3. When GPC analysis was performed using THF, the molecular weights of the polymer were in the same range but the average molecular weights appear to be slightly smaller: $M_n = 3700$, $M_w = 4700$ relative to polystyrene standards, $I = 1.4$. Moreover, a large peak due to **1** appeared, confirming a cleavage of the polymer in THF leading to **1**. The other signals observed at high elution times correspond to the dimesitylgermadiol $Mes_2Ge(OH)_2$ and dimesityl-

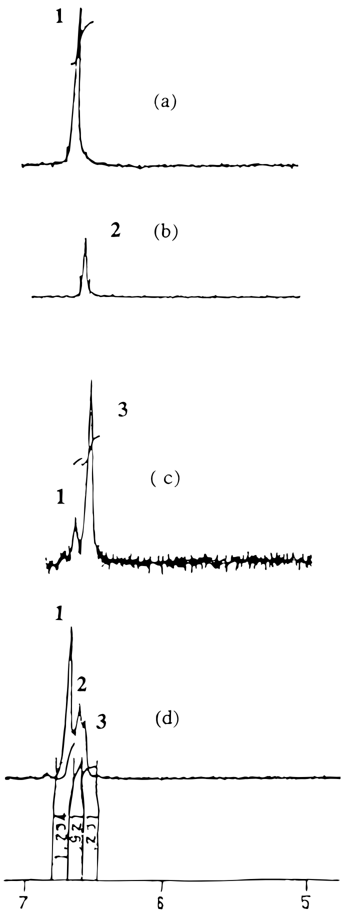


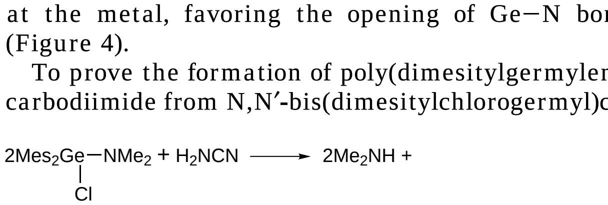
Figure 1. ^{1}H NMR identification of **1**, **2**, and **3** in a mixture (d) by comparison with recrystallized pure samples of **1** (a) and **2** (b). The purest sample of **3** (c) is obtained from Scheme 3, *iii*.

digermoxane $(Mes_2GeO)_2$, formed by hydrolysis of the moisture-sensitive Ge−N bonds.

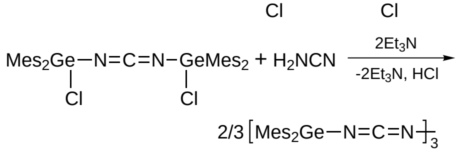
Attempted recrystallization of **2** and **3** led to the formation of **1,** which is also the only compound obtained after gentle heating or after a few days in THF solution (Scheme 2, *vi*) (Figure 3). However, we were able to partially recover thin white needles of tetramer **2** from $CHCl_3$ solution, which allowed an X-ray analysis of that compound. **3** could not be recovered from $CHCl_3$, and from benzene a sticky product was obtained.

The fact that in THF **2** and **3** were converted to **1** (n=3) is possibly due to nucleophilic assistance by THF at the metal, favoring the opening of Ge−N bonds (Figure 4).

To prove the formation of poly(dimesitylgermylene)carbodiimide from N,N′-bis(dimesitylchlorogermyl)carbodiimide (Scheme 2, *iv*, *vi*), we prepared the latter by transamination from (dimesitylchlorogermyl)dimethylamine (eq 1). Subsequent dehydrochlorination of the dichloride gave **1** (eq 2). However, although bis(dimesitylchlorogermyl)carbodiimide is the main product of the reaction (eq 1), part of the dimethylamine formed acts as a dehydrohalogenating agent and polymer **3** was also obtained as a byproduct (cf. Experimental Section).



$$2Mes_2\underset{|\atop Cl}{Ge}{-}NMe_2 + H_2NCN \longrightarrow 2Me_2NH + Mes_2\underset{|\atop Cl}{Ge}{-}N{=}C{=}N{-}\underset{|\atop Cl}{Ge}Mes_2 \qquad (1)$$



$$Mes_2\underset{|\atop Cl}{Ge}{-}N{=}C{=}N{-}\underset{|\atop Cl}{Ge}Mes_2 + H_2NCN \xrightarrow[-2Et_3N,\ HCl]{2Et_3N} 2/3\left[Mes_2Ge{-}N{=}C{=}N\right]_3 \qquad (2)$$

1

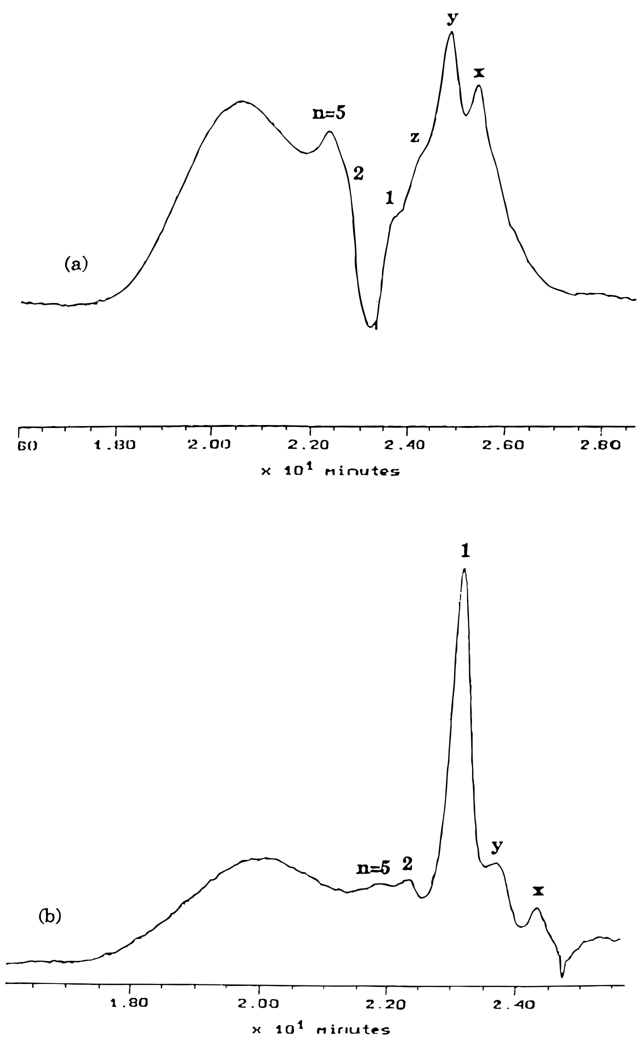
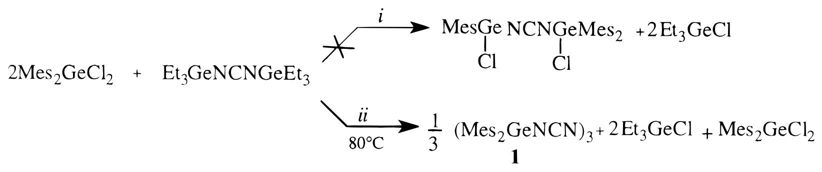


Figure 2. GPC traces of $(Mes_2GeNCN)_n$ **3** in (a) toluene solution and (b)THF solution. **1** (n = 3), **2** (n = 4), x = $Mes_2Ge(OH)_2$, y = $(Mes_2GeO)_2$, z = $(Mes_2GeO)_3$.

Bis(dimesitylchlorogermyl)carbodiimide cannot be isolated by an exchange reaction (Scheme 4, *i*). Ge−N/GeCl exchange, as in that reaction, requires heating and, therefore, led to formation of **1** (Scheme 4, *ii*); one-half of the starting dimesityldichorogermane remained unchanged.

X-ray Analysis of 1 and 2. X-ray analysis of trimer **1** gave the structure shown in Figure 5. The molecule is twisted into a propeller-like conformation, but with the overall structure possessing a center of symmetry, showing that a racemic mixture of the novel macrocycles had been formed. The diimine linkages are approximately linear as expected, with N−C bond lengths in the range 1.192(5)−1.221(6) Å and angles in the range 171.1(5)−173.6(5)°. The germanium centers adopt an unstrained tetrahedral geometry, with Ge−N bond lengths in the range 1.834(4)−1.855(3) Å and Ge−C distances in the range 1.942(4)−1.955(4) Å.

Scheme 4



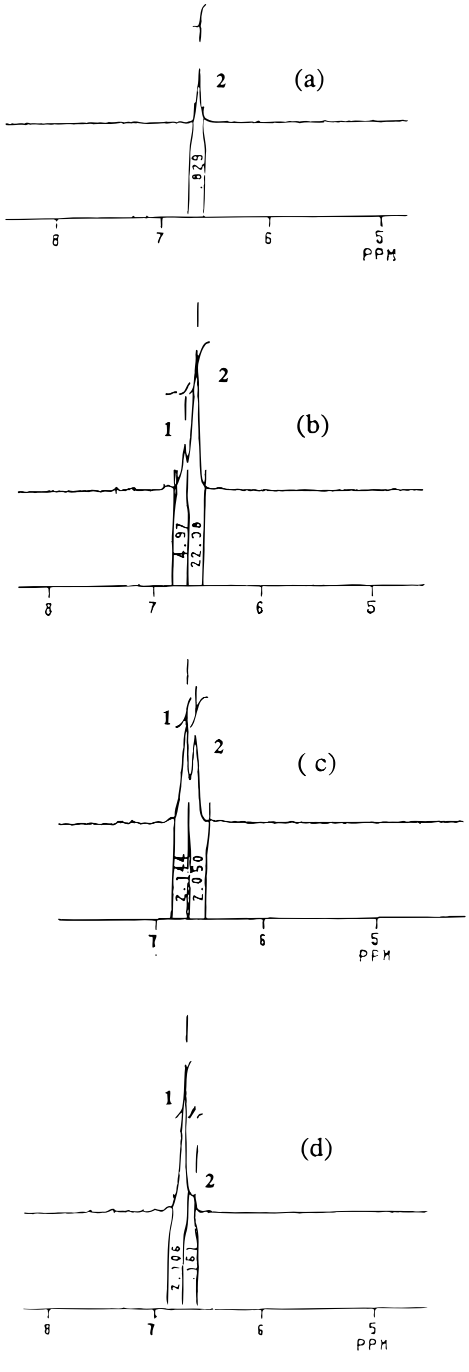


Figure 3. Example of the conversion of **2** to **1** at room temperature in THF solution: (a) **2** recrystallized in $CHCl_3$; (b) after 2 days in THF; (c) after 5 days; (d) after 8 days.

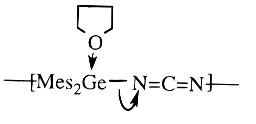


Figure 4.

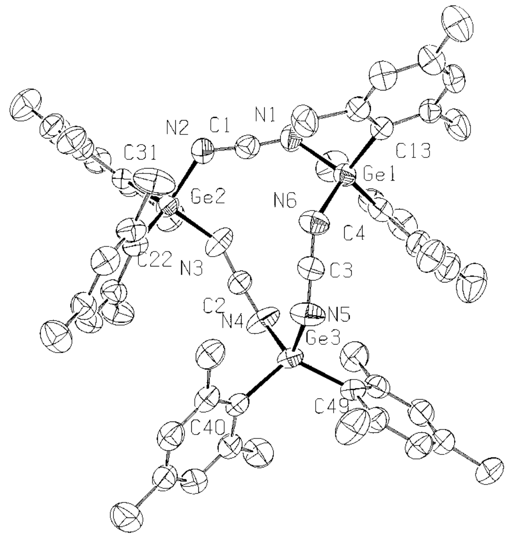


Figure 5. A single molecule of the germanium trimer **1** showing the numbering scheme for the germanium and nitrogen atoms. Thermal ellipsoids are shown at the 50% probability level.

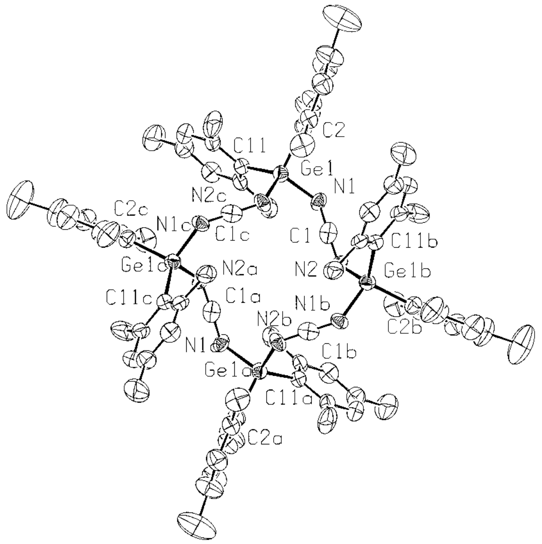


Figure 6. A single molecule of the germanium tetramer **2** showing the numbering scheme for the germanium and nitrogen atoms. Thermal ellipsoids are shown at the 50% probability level.

X-ray analysis of tetramer **2** gave the overall structure shown in Figure 6. This molecule crystallizes in the unusual space group $I\bar{4}$, with the tetrameric molecule possessing a $\bar{4}$ axis in the crystal. This high symmetry may be related to the high rigidity associated with the diimine and the mesityl groupings. The germanium center again adopts an unstrained tetrahedral geometry with Ge−N distances of 1.836(7) and 1.847(7) Å and Ge−C distances of 1.956(7) and 1.970(8) Å. The N−C−N

Table 1. Selected Bond Lengths (Å) and Angles (deg) for 1

Ge(1)−N(6)	1.847(4)	N(6)−Ge(1)−N(1)	101.98(17)
Ge(1)−N(1)	1.855(3)	N(6)−Ge(1)−C(13)	108.90(16)
Ge(1)−C(13)	1.942(4)	N(1)−Ge(1)−C(13)	105.24(17)
Ge(1)−C(4)	1.945(4)	N(6)−Ge(1)−C(4)	108.98(17)
Ge(2)−N(3)	1.843(4)	N(1)−Ge(1)−C(4)	112.30(17)
Ge(2)−N(2)	1.843(4)	C(13)−Ge(1)−C(4)	118.18(16)
Ge(2)−C(22)	1.944(4)	N(3)−Ge(2)−N(2)	99.38(18)
Ge(2)−C(31)	1.955(4)	N(3)−Ge(2)−C(22)	110.35(18)
Ge(3)−N(5)	1.834(4)	N(2)−Ge(2)−C(22)	113.19(17)
Ge(3)−N(4)	1.848(4)	N(3)−Ge(2)−C(31)	111.91(17)
Ge(3)−C(49)	1.943(4)	N(2)−Ge(2)−C(31)	105.78(16)
Ge(3)−C(40)	1.949(4)	C(22)−Ge(2)−C(31)	115.09(16)
		N(5)−Ge(3)−N(4)	106.43(19)
		N(5)−Ge(3)−C(49)	103.5(2)
		N(4)−Ge(3)−C(49)	114.43(17)
		N(5)−Ge(3)−C(40)	113.80(17)
		N(4)−Ge(3)−C(40)	104.38(19)
		C(49)−Ge(3)−C(40)	114.35(16)

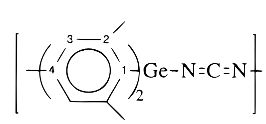
Table 2. Selected Bond Lengths (Å) and Angles (deg) for 2

Ge(1)−N(2)	1.836(7)	N(2)−Ge(1)−N(1)	103.4(3)
Ge(1)−N(1)	1.847(7)	N(2)−Ge(1)−C(11)	107.8(3)
Ge(1)−C(11)	1.956(7)	N(1)−Ge(1)−C(11)	113.1(3)
Ge(1)−C(2)	1.970(8)	N(2)−Ge(1)−C(2)	114.6(3)
		N(1)−Ge(1)−C(2)	105.1(3)
		C(11)−Ge(1)−C(2)	112.5(3)
		C(7)−C(2)−C(3)	119.8(8)
		C(7)−C(2)−Ge(1)	118.4(6)
		C(3)−C(2)−Ge(1)	121.7(6)
		C(1)−N(1)−Ge(1)	130.0(6)

angle is 173.5(9)°, and the two C−N distances are 1.128(10) and 1.200(11) Å. Both molecules therefore display a geometrical consistency. Selected bond lengths and angles are shown in Table 1 for **1** and in Table 2 for **2**.

Experimental Section

All syntheses were performed in dry solvents under a dry nitrogen atmosphere using standard Schlenk techniques. The compounds were characterized by the usual analytical techniques: IR Perkin-Elmer 1600 FT; ^{1}H NMR (80 MHz), AC 80 Bruker; ^{13}C NMR (50.3 MHz), AC 200, δ ppm/TMS. For the dimesitylgermylenecarbodiimides, the following numbering system was adopted



Mass spectroscopy: Ribermag R1010 (DCi/CH$_4$), Perkin-Elmer SCIEX API 100 (APCI = atmospheric-pressure chemical ionization, eluant CH$_3$CN, solvent benzene), and HP 5989 (Ei). GPC analysis was performed on three Waters Styragel HR columns (10^{-2}, 10^{-1},1 μ), refractive index detection, with THF or toluene as the eluant (1.2 mL/min) versus polystyrene standards for high molecular weight compounds and versus pure samples of Mes$_3$GeN=C=NGeMes$_3$[11] (M = 900), **1** (M = 1052), **2** (M = 1404), and standards for low molecular weight compounds. Elemental analysis was performed by the Microanalysis Center of Ecole Nationale Superieure de Chimie de Toulouse. Dimesityldichlorogermane was prepared according to literature.[13] Other chemicals were purchased from Aldrich Chemical Co.

Preparation of Tris(dimesitylgermylenecarbodiimide) (1). To cyanamide (0.31 g, 7.4 mmol) in solution in 10 mL THF with Et$_3$N (1.02 g, 10.09 mmol) was added dropwise with stirring a solution of Mes$_2$GeCl$_2$ (0.91 g, 2.4 mmol) in 11 mL of THF. After 18 h of stirring at room temperature, THF was replaced by benzene (8 mL) and triethylamine hydrochloride was filtered. Evaporation of the filtrate in vacuo gave a white powder of crude **1**. Recrystallization from benzene gave 0.62 g of pure **1**, mp 168 °C (yield 74%; recrystallization can also be performed from hexane or ether).

^{1}H NMR (CDCl$_3$): δ 2.22 (s, 18H, p-CH$_3$), 2.30 (s, 36H, o-CH$_3$), 6.71 (s, 12H, CH). ^{13}C NMR (CDCl$_3$): δ 21.13 (p-CH$_3$), 23.16 (o-CH$_3$); 132.32 (C$_1$), 142.96 (C$_2$), 129.41 (C$_3$), 139.60 (C$_4$), 134.15 (NCN). IR: (CDCl$_3$) (ν_{as}(NCN)): 2144 cm^{-1}; (Nujol) 2133 cm^{-1}. MS (DCi/CH$_4$, m/z): 1053 (100, (M + 1)$^+$), 1081 (12, (M + 29)$^+$), and a small amount of tetramer **2** (1405 (10, (M + 1)$^+$)). Anal. Calcd for C$_{57}$H$_{66}$ N$_6$Ge$_3$: C, 65.02; H, 6.32; N, 7.98. Found: C, 64.95; H, 6.23; N, 7.71.

Crystal Data for 1, $C_{57}H_{66}N_6Ge_3$. M = 1052.984. Triclinic, $P\bar{1}$ (No. 2). a = 13.193(5) Å, b = 15.729(5) Å, c = 15.923(5) Å, α = 107.32(6)°, β = 112.61(5)°, γ =105.76(6)°. V = 2617.6 Å,^{3} Z = 2, ρ_c = 1.265 Mg m^{-3}, μ = 2.308 mm^{-1}. F(000) = 1012. T = 293 K. λ (Mo Kα) = 0.710 73 Å.

The data were collected on a small Mar Research image plate system using 3 kW sealed-tube molybdenum radiation (T = 293 K). Exposure time was 2 min per frame, and 95 2° frames were collected. No correction for absorption was applied, and decay was negligible. Data were processed with the Mar Research version of Wolfgang Kabsch's program XDS. Cell constants were determined using the GLOREF routine in XDS. The structure was solved using direct methods and confirmed by Patterson methods refining on intensities to give R1 = 0.0561, wR2 = 0.1673 for 7664 unique observed reflections. The refinement was based on F^2. The programs SHELXS96 and SHELXL96 were used for all calculations. Hydrogen atoms were placed geometrically using the riding model with thermal parameters set to 1.5 times that for the atom to which the hydrogen is attached. The diagram was drawn with PLATON. The data have been deposited with the Cambridge Crystallographic Data Centre.

Characterization of Bis(dimesitylchlorogermyl)carbodiimide. (1) Reaction of Mes$_2$GeCl$_2$ with H$_2$NCN (Schemes 2 and 3). To Mes$_2$GeCl$_2$ (0.90 g, 2.38 mmol) in 8 mL of THF was added dropwise at room temperature a solution of H$_2$NCN (0.05 g, 1.19 mmol) and Et$_3$N (0.24 g, 2.38 mmol) in 5 mL of THF. After 2 h of stirring, THF was replaced by benzene and [Et$_3$NH]Cl was filtered. ^{1}H NMR analysis of the white residue obtained by evaporating the solvent in vacuo showed the presence of Mes$_2$GeCl$_2$ (50%), **1** (25%), and Mes$_2$(Cl)GeN=C=NGe(Cl)Mes$_2$ (25%), the latter identified by comparison with a sample formed according to eq 1.

(2) Reaction of Lithium Cyanamide with Mes$_2$GeCl$_2$ (Scheme 3). Lithium cyanamide was prepared by dropwise addition of t-BuLi (1.7 M in pentane, 2.38 mmol, 1.4 mL) with stirring to H$_2$NCN (0.05 g, 1.19 mmol) in 3 mL of THF at −60 °C. The mixture was allowed to warm to room temperature with stirring for 30 min. This solution was added with stirring to Mes$_2$GeCl$_2$ (0.9 g, 2.38 mmol) in 7 mL of THF at −60 °C. After 2 h at room temperature, THF was replaced by benzene and LiCl was separated by centrifugation. Evaporation of the solvent gave a white residue whose ^{1}H NMR analysis showed the presence of Mes$_2$GeCl$_2$ (25%), **1** (9%), **2** (28%), and Mes$_2$Ge(Cl)N=C=NGe(Cl)Mes$_2$ (38%).

Preparation of 1 by Transmetalation. To lithium cyanamide (1.19 mmol in 5 mL of THF) prepared as before was added Mes$_2$GeCl$_2$ (0.45 g, 1.17 mmol) in 6 mL of THF, at room temperature with stirring. After replacement of THF by benzene, centrifugation of LiCl, and evaporation of benzene, 0.32 g of **1** (yield 78%) was obtained.

Preparation of Tetrakis(dimesitylgermylenecarbodiimide) (2). A solution of H$_2$NCN (0.10 g, 2.38 mmol) and

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(13) Rivière, P.; Rivière-Baudet, M. *Organomet. Synth.* **1988**, *4*, 542.

Et_3N (0.48 g, 4.76 mmol) in 7 mL of THF was added dropwise with stirring to Mes_2GeCl_2 (0.90 g, 2.36 mmol) in 10 mL of THF at −60 °C. The mixture was allowed to warm to room temperature, THF was replaced by benzene and $[Et_3NH]Cl$ was filtered. Evaporation of benzene gave 0.45 g (yield 54%) of a white residue analyzed by ^1H NMR to be composed of **1** (53%), **2** (38%), and **3** (9%). Slow recrystallization from chloroform (10 mL) at room temperature afforded 0.08 g of white needles of pure **2,** mp 265 °C (yield 2%).

^1H NMR ($CDCl_3$): δ 2.22 (s, 72H, *o*, *p*-CH_3), 6.66 (s, 16H, CH). ^{13}C NMR ($CDCl_3$): δ 21.07 (*p*-CH_3), 22.98 (*o*-CH_3), 132.89 (C_1), 142.94 (C_2), 129.27 (C_3), 139.26 (C_4), 134.61 (NCN). IR: ($CDCl_3$) (ν_{as}NCN) 2122 cm^{-1}; (Nujol) 2122 cm^{-1}. MS (DCi/CH_4, *m/z*): 1405 (100, $(M + 1)^+$). Anal. Calcd for $C_{76}H_{88}N_8Ge_4$: C, 65.02; H, 6.32; N, 7.98. Found: C, 64.71; H, 5.96; N, 7.92.

The remaining solution contained only **1** (^1H NMR analysis, **3** was converted to **1**). Evaporation in vacuo gave 0.35 g of **1** (yield 43%).

Crystal Data for 2, $(C_{19}H_{22}N_2Ge)_4$. $M = 1323.36$. Tetragonal, $I\bar{4}$ (No. 82). $a = 20.779(5)$ Å, $b = 20.779(5)$ Å, $c = 8.615\ (3)$ Å. $V = 3719.7$ Å^3. $Z = 2$, $\rho_c = 1.738$ Mg m^{-3}, $\mu = 4.824$ mm^{-1}, $F(000) = 1908$. $T = 293$K, λ (Mo Kα) = 0.710 73 Å.

The data were collected on a small Mar Research image plate system using 3 kW sealed-tube molybdenum radiation ($T = 293$ K). Exposure time was 10 min per frame, and 95 2° frames were collected. No correction for absorption was applied, and decay was negligible. Data were processed with the Mar Research version of Wolfgang Kabsch's program XDS. Cell constants were determined using the GLOREF routine in XDS. The structure was solved using direct methods and confirmed by Patterson methods refining on intensities to give R1 = 0.0606, wR2 = 0.1724 for 1937 unique observed reflections. The refinement was based on F^2. The programs SHELXS96 and SHELXL96 were used for all calculations. Hydrogen atoms were placed geometrically using the riding model with thermal parameters set to 1.5 times that for the atom to which the hydrogen is attached. The diagram was drawn with PLATON. The data have been deposited with the Cambridge Crystallographic Data Centre.

Preparation of 3. To Mes_2GeCl_2 (0.90 g, 2.36 mmol) in 15 mL of THF was added dropwise over 30 min with stirring at −70 °C lithium cyanamide (2.36 mmol) as a suspension in 10 mL of THF. The mixture was stirred at −70 °C for 1.5 h. The THF was evaporated and immediately replaced by benzene. Lithium chloride was separated by centrifugation. The remaining solution was evaporated in a vacuum, leaving 0.71 g of a white amorphous residue of **3** (containing 10−15% of **1**) (yield 85%). **3** dissolved in benzene was reprecipitated by addition of pentane. mp 100−110 °C (dec).

^1H NMR ($CDCl_3$): δ 2.17 (s, *p*-CH_3), 2.10 (s, *o*-CH_3), 6.58 (s, CH). ^{13}C NMR: ($CDCl_3$) δ 21.12 (*p*-CH_3), 22.93 (*o*-CH_3), 132.87 (C_1), 142.72 (C_2), 129.26 (C_3), 139.10 (C_4), 132.00 (NCN); (C_6D_6) δ 21.17 (*p*-CH_3), 23.37 (*o*-CH_3), 133.47 (C_1), 143.14 (C_2), 129.84 (C_3), 139.37 (C_4). IR ($CDCl_3$): (ν_{as}NCN) 2108 cm^{-1}. MS (DCi/CH_4, *m/z*): $(Mes_2GeNCN)_5$ 1755 (5, $(M + 1)^+$), $(Mes_2GeNCN)_4$ 1405 (25, $(M + 1)^+$), $(Mes_2GeNCN)_3$ 1053 (100, $(M + 1)^+$). APCI: $(Mes_2GeNCN)_6$ 2106 ($(M + 1)^+$), $(Mes_2GeNCN)_5$ 1755 ($(M + 1)^+$). Anal. Calcd for $(C_{19}H_{22}N_2Ge)_n$: C, 65.02; H, 6.32; N, 7.98. Found: C, 64.67; H, 6.34; N, 7.53.

All attempts to recrystallize **3** from ether or chloroform gave **1**; in benzene a sticky material was obtained. GPC analysis in toluene: large, broad signal corresponding to a mass distribution from $4 < n \cong 30$ (polystyrene standard).

Conversions of 2 and 3 in THF and Benzene Solution. (a) Solutions of pure **2** or **3** in THF (≅0.2 mg in 6 mL of THF) were placed in sealed tubes. Each tube was either heated or kept at room temperature before analysis. Then after opening the tube, the THF was evaporated in vacuo and replaced by $CDCl_3$ for ^1H NMR analysis. The results are as follows: **2** or **3** after 3 h at 80 °C were completely converted to **1**; conversion of **2** at room temperature, percent of **1** formed after 1 day (5%), 2 days (17%), 5 days (53%), 8 days (92%) (Figure 3); conversion of **3** at room temperature, percent of **1** formed after 1 day (10%), 2 days (15%), 5 days (69%), 8 days (97%). (b) In benzene solution: A solution of **3** in benzene either heated for 3 h at 90 °C or after 1 week at room temperature did not show any change.

Conversion of 3 in the Presence of Excess Cyanamide. A solution of **3** (0.2 mg/6 mL of THF) in the presence of an excess of cyanamide (4 mol equiv) gave 10% of **1** after 18 h of stirring at room temperature.

A solution of **3** (0.2 mg/6 mL of C_6H_6) in the presence of an excess of cyanamide in suspension (4 mol equiv) after 18h of stirring at room temperature gave 10% of **1**.

Reaction of Solutions of 2 and 3 with Air. The same solution of **2** or **3** (in THF or benzene) kept at room temperature in an open flask led slowly, by hydrolysis, to the formation of $Mes_2Ge(OH)_2$ and $(Mes_2GeO)_n$ ($n = 2$, 3), characterized by ^1H NMR and GPC (Figure 2), by cleavage of the moisture-sensitive Ge−N bonds.

Preparation of Bis(dimesitylchlorogermyl)carbodiimide by Transamination from $Mes_2Ge(Cl)NMe_2$ (eq 1). (1)Preparation of $Mes_2Ge(Cl)NMe_2$. To Mes_2GeCl_2 (0.9 g, 2.36 mmol) in 7 mL of THF was added dropwise, at room temperature with stirring, Me_2NLi (2.36 mmol in THF). After an additional 2 h of stirring at room temperature, THF was replaced by benzene and LiCl separated by centrifugation. Evaporation of benzene in vacuo led to a white, sticky compound (0.68 g) identified by ^1H and ^{13}C NMR as pure $Mes_2Ge(Cl)NMe_2$. Yield: 74%.

^1H NMR ($CDCl_3$): δ 2.25 (s, 6H, *p*-CH_3), 2.39 (s, 12H, *o*-CH_3), 6.82 (s, 4H, CH), 2.61 (s, 6H, NMe_2). ^{13}C NMR ($CDCl_3$): δ 21.07 (*p*-CH_3), 23.16 (*o*-CH_3), 133.73 (C_1), 143.18 (C_2), 129.66 (C_3), 139.83 (C_4), 39.72 (NMe_2). MS (Ei, *m/z*): 391 (2, ($M^{+\bullet}$)), 356 (5, ($M^{+\bullet} - Cl$)), 346 (25, ($M^{+\bullet} - Me_2NH$)).

(2) Transamination. To $Mes_2Ge(Cl)NMe_2$ (0.92 g, 2.36 mmol) in 4 mL of THF was added H_2NCN (0.049 g, 1.18 mmol) in 2 mL of THF dropwise at room temperature with stirring. There was immediate evolution of dimethylamine. After a few minutes, a light precipitate of $[Me_2NH_2]Cl$ was formed. After 2 h of stirring, THF was replaced by benzene and dimethylamine hydrochloride was removed by centrifugation. Evaporation of solvents in vacuo gave a white, amorphous powder (0.61 g) (mp 136 °C) of $Mes_2(Cl)GeN{=}C{=}NGe(Cl)Mes_2$ (containing $(Mes_2GeNCN)_n$ **3** (∼ 35%)), starting material for **1** thereafter.

Spectral characteristics of $Mes_2(Cl)GeN{=}C{=}NGe(Cl)Mes_2$. ^1H NMR ($CDCl_3$): δ 2.22 (s, 36H, *o*-CH_3−*p*-CH_3), 6.72 (s, 8H, CH). ^{13}C NMR ($CDCl_3$): δ 21.08 (*p*-CH_3), 22.68 (*o*-CH_3), 143.43 (C_2), 129.16 (C_3), 138.90 (C_4). IR ($CDCl_3$): (ν_{as}NCN) 2111 cm^{-1}. MS (DCI/CH_4, *m/z*): 733 (5, $(M + 1)^+$).

Formation of 1 from Bis(dimesitylchlorogermyl)carbodiimide (eq 2). The white powder of $Mes_2(Cl)GeN{=}C{=}NGe(Cl)Mes_2$ containing ∼35% of **3**, prepared above, was dissolved in 4 mL of THF and treated with an excess of cyanamide (0.1 g, 2.36 mmol) in 2 mL of THF. Et_3N (0.48 g, 4.72 mmol) was added, and the mixture was stirred for 1 h at room temperature. After replacement of THF with C_6H_6 to remove $[Et_3NH]Cl$, evaporation of the solvent gave 0.38 g of **1** as a white powder containing 18% of **3**. Yield 81%.

Formation of 1 by an Exchange Reaction (Scheme 4). To Mes_2GeCl_2 (0.88 g, 2.32 mmol) in 5 mL of THF was added $Et_3GeN{=}C{=}NGeEt_3$[11] (0.42 g, 1.16 mmol) in 5 mL of THF. Et_3GeCl formation was monitored by gas chromatography and required 16 h of heating at 80 °C for completion. After evaporation of the solvent, triethylchlorogermane was distilled in vacuo. ^1H NMR analysis of the white residue (0.78 g) showed the quantitative formation of **1**. Higher oligomers **2** and **3** cannot be obtained in these experimental conditions.

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Supporting Information Available: Tables giving crystal data and structure refinement details, positional and thermal parameters, and bond distances and angles for **1** and **2** (18 pages). Ordering information is given on any current masthead page.

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