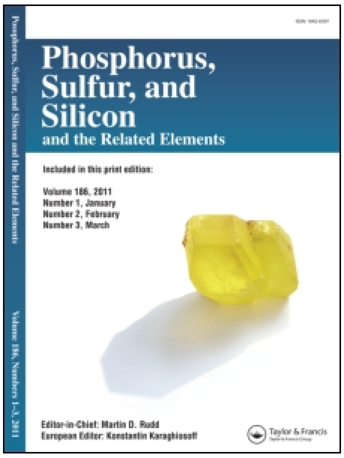

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TRIMESITYLGERMYLCARBODIIMIDE LITHIUM, PRECURSOR FOR NEW MIXED POLYMETALLATED CARBODIIMIDE AND POLYCARBODIIMIDES OF Ge, Si, Sb

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TRIMESITYLGERMYLCARBODIIMIDE LITHIUM, PRECURSOR FOR NEW MIXED POLYMETALLATED CARBODIIMIDE AND POLYCARBODIIMIDES OF Ge, Si, Sb

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Trimesitylgermylcarbodiimide lithium characterized in the reaction of trimesitylgermylchloride on dilithium cyanamide, is the starting material to stable germylsilyl or unsymetric digermylcarbodiimides. The non hindered Ge-N bond of triethylgermylcarbodiimide is cleaved by t-butyllithium providing another route to unsymetric N-triethylgermyl-N'-silylcarbodiimide.

Trimesitylgermylcarbodiimide lithium reacts with metal dihalides yielding trimetalled (Ge, Sb) dicarbodiimides. X-ray structure of bis(trimesitylgermylcarbodiimido)diethylgermane confirms the inequivalence of the two carbodiimides groups observed by infrared spectroscopy.

N-diethylchlorogermyl-N'-trimesitylgermylcarbodiimide with dilithium cyanamide leads to a tetragermyltricarbodiimide: the bis(N-diethylgermyl-N'-trimesitylgermylcarbodiimido)-carbodiimide, in which inequivalence of the ethyl groups can be explained by the steric hindrance of terminal trimesitylgermyl carbodiimido groups.

Keywords: trimesitylgermylcarbodiimide lithium; dimetallated carbodiimides; silyl and stibyl germylcarbodiimides; metallated polycarbodiimides; polygermylpolycarbodiimides

INTRODUCTION

Being interested in the synthesis of new polymers within the series of germylcarbodiimides[1], we tried to find a general method to lengthen the

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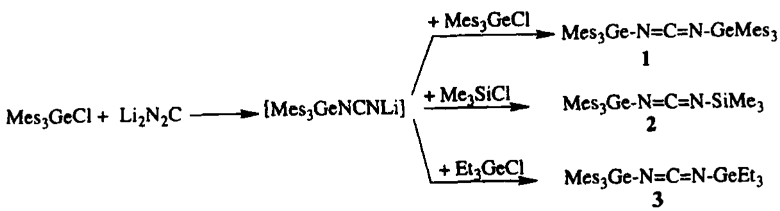
chains of germylcarbodiimides using either a lithium or an halogen as terminal group.

RESULTS AND DISCUSSION

We recently characterized triethyl- and trimesityl- monogermylcyanamides[2,3] and isolated the symmetrical bis(trimesitylgermyl)carbodiimide **1** either by dehydrohalogenation between trimesitylchlorogermane and cyanamide or by ransmetallation[2]. Actually the latter reaction can be achieved in two steps, the first one (scheme 1) leading to the trimesitylgermyl carbodiimide lithium intermediate characterized through the formation of unsymmetrical N, N'-dimetallated carbodiimides **2** and **3** (scheme 1).



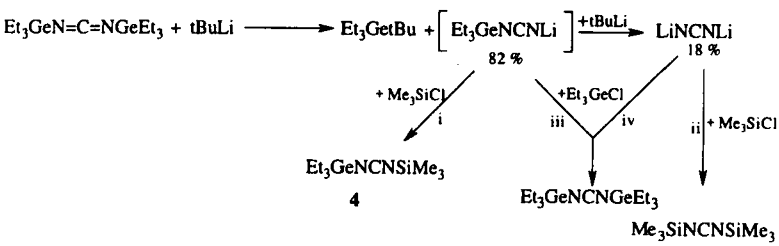
SCHEME 1

Contrary to non hindered trimethylgermylsilylcarbodiimides[4,5] which usually are unstable and tend to rearrange into symmetric derivatives, the trimesitylgermyl compounds **2** and **3** are stable compounds. To observe the rearrangement of **3** into **1** and bis(triethylgermyl)carbodiimide[6], **3** has to be heated for three days at 100°C (eq. 1).

$$\underset{\mathbf{3}}{2\,Mes_3Ge\text{-}N{=}C{=}N\text{-}GeEt_3} \xrightarrow[100°C]{3\ days} Et_3GeNCNGeEt_3 + \underset{\mathbf{1}}{Mes_3GeNCNGeMes_3} \quad \text{(eq. 1)}$$

Although Ge-N bonds are usually very stable in the presence of organolithium or magnesium derivatives[7,8], we found that bis(triethylgermyl)carbodiimide is easily cleaved by t-butyllithium, providing another route to unsymmetric dimetallated N-germyl, N'-silylcarbodiimide, after treatment by trimethylchlorosilane (scheme 2, i). However, the reaction leads also partially to dicleavage, and disilylcarbodiimide (< 20%) is also obtained (scheme 2, ii). Of course, when the reaction with t-butyllithium is followed by addition of triethylchlorogermane, the starting compound is obtained besides triethyl-t-butylgermane (scheme 2, iii, iv). However, steric hindrance prevents the same cleavage reaction of Ge-N bonds in bis(trimesitylgermyl)carbodiimide, preventing the formation of trimesitylgermylcarbodiimide lithium which must be prepared according to scheme 1.

Note that **4** was previously obtained through an exchange reaction between bis(triethylgermyl)carbodiimide and trimethylchlorosilane[9] and that a similar cleavage of bis(trimethylsilyl)carbodiimide by LDA was previously observed[10,11].



SCHEME 2

Starting from trimesitylgermylcarbodimide lithium (scheme 1), if a dialkylgermyldichloride is used in the second step of the reaction instead of a monohalide, the reaction leads to a digermane carbodiimide with an halogermyl group at the end of the chain (eq. 2).

$$[Mes_3GeNCNLi] + Et_2GeCl_2 \longrightarrow LiCl + \underset{\mathbf{5}}{Mes_3Ge\text{-}N{=}C{=}N\text{-}GeEt_2Cl} \quad \text{(eq. 2)}$$

A longer chain is then easily obtained by duplication over dilithium cyanamide (eq. 3).

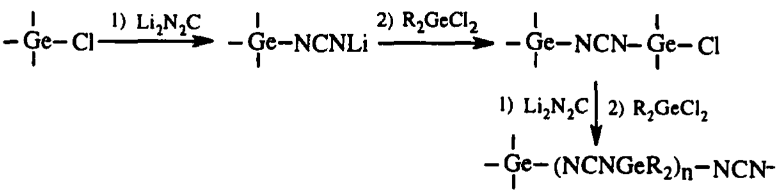
$$2\ \underset{\mathbf{5}}{Mes_3Ge\text{-}N{=}C{=}N\text{-}GeEt_2Cl} \xrightarrow[-\,2\,LiCl]{+\,Li_2N_2C} \underset{\mathbf{6}}{Mes_3GeNCNGeEt_2NCNGeEt_2NCNGeMes_3} \quad \text{(eq. 3)}$$

Lengthening of the chain can also be achieved from germylcarbodiimide lithium derivatives by metal bridges, according to equations 4 and 5.

$$2\,[Mes_3GeNCNLi] + Et_2GeCl_2 \xrightarrow{-2LiCl} \underset{\mathbf{7}}{Mes_3GeNCNGeEt_2NCNGeMes_3} \quad \text{(eq. 4)}$$

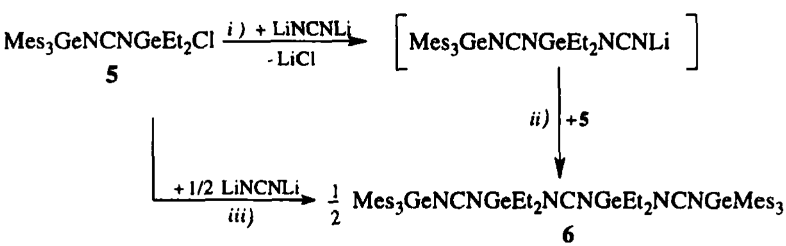
$$2\,[Mes_3GeNCNLi] + MesSbCl_2 \xrightarrow{-2LiCl} \underset{\mathbf{8}}{Mes_3GeNCNSbMesNCNGeMes_3} \quad \text{(eq. 5)}$$

Therefore, we thought that it would be possible to propose a general method for the lengthening of germylcarbodiimide chains by a GeNCN group, step by step, by successive alternative additions of Li_2N_2C and R_2GeX_2 (scheme 3).



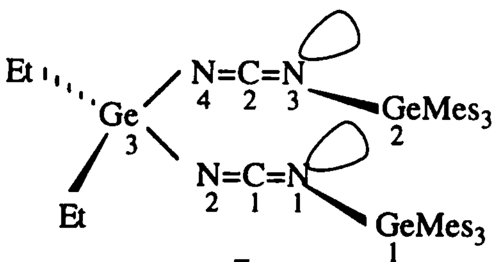
SCHEME 3

However from compound **5**, the addition of dilithium cyanamide did not lead to the expected dicarbodiimido lithium compound (scheme 4, i) but to the tetragermyl derivative **6**, half of the dilithium cyanamide remaining in solution. Most probably the lithium derivative of **5** as soon as formed reacts with the starting material **5** yielding **6** (scheme 4, ii).



SCHEME 4

All the metal cyanamides prepared were characterized by spectrochemical means. The monocarbodiimido compounds **3** and **5** present the characteristic absorption of the N=C=N group in infrared spectroscopy (2135 cm^{-1} and 2140 cm^{-1} respectively) while the dicarbodiimido compound **7** in solution exhibits two absorptions (2119 and 2171 cm^{-1}, $CDCl_3$). Since a cyanamide form with one nitrogen bearing two germyl groups is highly improbable[10,12,13,14], the two absorptions can be taken as an evidence for a different spatial arrangement in solution of the two carbodiimide groups in that molecule (figure 1).



7

FIGURE 1 Dicarbodiimido compound **7**

In the solid state, infrared analysis of **7** shows also two absorptions (2119 and 2155 cm^{-1}). An X-ray analysis of **7**, similarly to other germylcarbodiimides[1], [2], [3]shows almost linear NCN groups, born here by a tetrahedral central germanium atom (figure 2). Actually the measured distances N2Ge2 and N4Ge1 are different: 5.60 and 6.58 Å respectively which can explain the inequivalence of the NCN groups and the infrared absorptions observed. Selected bond lengths and angles for **7** are given in table I. Note that we found that molecular modelisation (cf. experimental) for the more stable conformer of **7** (35.04 Kcal/mol) (program Biosym. Insight II discover$_3$, force field ESFF) is in good concordance with the RX structure given figure 2.

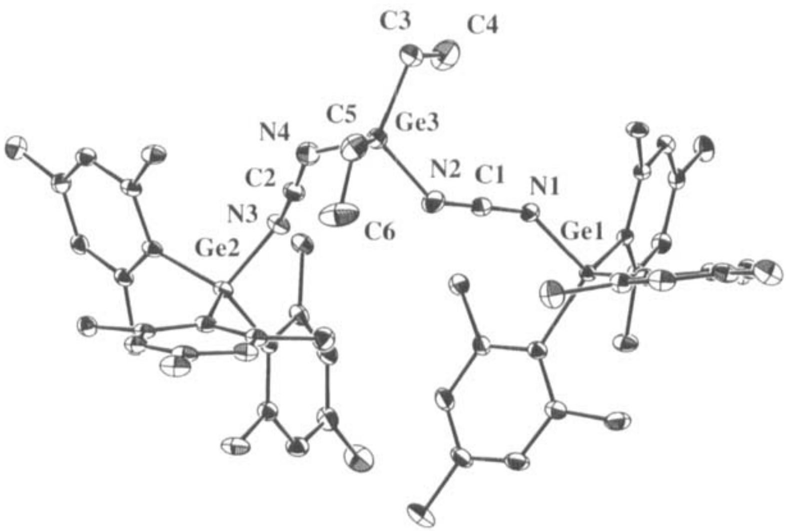


FIGURE 2 molecular structure of **7**

TABLE I RX diffractometry: selected bond lengths (Å) and angles (°) for **7**

G1N1	1.849 (3)	N1C1N2	177.5 (4)
Ge2N3	1.861 (3)	N3C2N4	174.1 (4)
Ge3N2	1.831 (3)	Ge1N1C1	141.7 (2)
Ge3N4	1.826 (3)	Ge2N3C2	137.8 (3)
N1C1	1.199 (4)	Ge3N4C2	135.0 (3)
C1N2	1.213 (5)	Ge3N2C1	136.6 (3)
N3C2	1.197 (4)	N2Ge3C3	110.1 (2))
C2N4	1.221 (5)	N2Ge3C5	107.4 (2)
		N2Ge3N4	107.0 (2)
		C5Ge3C3	115.1 (2)
		C5Ge3N4	107.9 (2)
		C3Ge3N4	109.0 (2)

The tetragermyltricarbodiimide **6** displays a very strong and broad NCN absorption in infrared spectroscopy(2188–2055 cm^{-1}). In ^{13}C NMR we noted two sets of ethyl groups, which therefore must have different surrounding. However we did not obtain monocrystals of **7** and the X-ray analysis could not be performed but, on the molecular modelisation (figure 3) (program Biosym. Insight II discover$_3$, force field ESFF) for the more stable conformer of **6** (35.62 Kcal/mol) (figure 3), we can note that two ethyl groups (one on each germanium of the central chain) are about 5.7 Å of the next trimesitylgermyl terminal group while the two others are about 7.1 Å of the same terminal groups [distances (Å): Ge1Et1: 5.48 (CH_3); 5.95 (CH_2); Ge4Et1′: 5.46 (CH_3); 6.12 (CH_2); Ge1Et2: 7.14 (CH_3); 6.96 (CH_2); Ge4Et2′: 7.28 (CH_3); 7.01 (CH_2)].

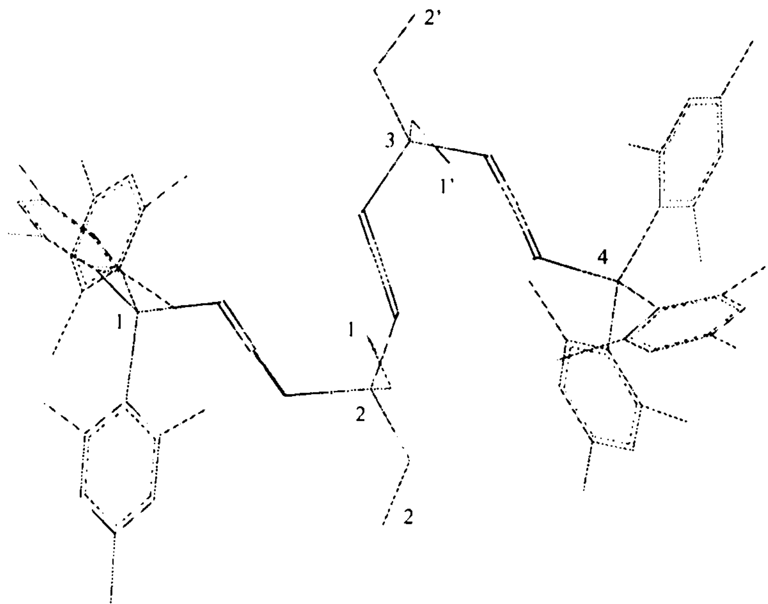


FIGURE 3 Molecular modelisation for **6** *(program Biosym, Insight II discover$_3$, force field ESFF)*

EXPERIMENTAL

All reactions were carried out under nitrogen or argon and with dry solvents. NMR spectra were recorded on Brucker AC 80 (^1H) and AC 200 spectrometers (^{13}C; in the sequence Jmod.) (δ ppm/TMS); IR spectra on a Perkin-Elmer 1600 FT IR spectrometer; Gas Chromatography: Hewlett Packard 6890 GC (column HP1, Methylsilicon); mass spectra on a 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/CH_4). Melting points were measured on a Leitz microscope. The numbering of ^{13}C is given in Figure 4.

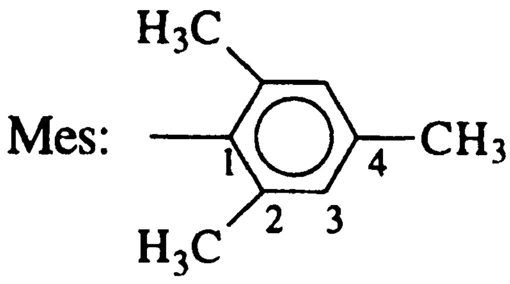


FIGURE 4 ^{13}C numbering used for aromatic carbons in mesityl groups

Preparation of $Mes_3GeNCNGeMes_3$ (1) (see ref.[2])

To H_2NCN (0.07g, 1.72mmol) in 4mL of THF at −70°C, was added dropwise under stirring a solution of tBuLi in pentane (3.44mmol, 2.02mL at 1.7M). After 30mn at room temperature, the dilithium cyanamide is cooled again at −60°C and Mes_3GeCl (0.8g, 1.72mmol) in 6mL of THF is added dropwise under stirring at −60°C.After 1h hour at the same temperature the same amount of Mes_3GeCl is added (0.8g, 1.72mmol, in 6mL of THF). The Schlenk tube is then slowly warmed to room temperature and warmed further at 50°C for 3h. THF was replaced by benzene and LiCl separated by centrifugation. Evaporation of the solvents under vacuo afforded 1.31g of **1** (conform to ref.[2]) (yield 85%).

Preparation of $Mes_3GeNCNSiMe_3$ (2)

To dilithium cyanamide (0.75 mmol) prepared as for **1**, in suspension in 4 mL of THF was added dropwise under stirring at −60 °C trimesitylchlorogermane (0.35 g, 0.75 mmol) in 3mL of THF. After 1h stirring at −60 °C, Me_3SiCl (0.10 g, 0.92 mmol) was added to the suspension of $Mes_3GeNCNLi$. After 10 mn at −60°C, the Schlenk tube was allowed to warm to room temperature for 2 h. THF was replaced by benzene and the lithium chloride was separated by centrifugation. The remaining solvent was evaporated under vacuo leading to 0.32 g of **2** as a yellow sticky compound (yield 81 %). ^{1}H NMR ($CDCl_3$): δ 2.28 (s, 27H, pCH_3+oCH_3); 6.85 (s, 6H, C_6H_2); 0.07 (s, 9H, $SiMe_3$). ^{13}C NMR ($CDCl_3$): δ 21.09 (pCH_3); 23.92 (oCH_3); 136.38 (C_1); 143.34 (C_2); 129.55 (C_3); 138.90 (C_4); 1.55 ($SiMe_3$). IR ($CDCl_3$): 2162 cm^{-1} (NCN). MS (EI, m/z,%): 544, 21% (M^{+}.); 529, 11% (M^{+}.-Me).

Preparation of $Mes_3GeNCNGeEt_3$ (3)

To $Mes_3GeNCNLi$ (0.75 mmol) in 7 mL of THF, prepared as before, was added dropwise under stirring at −60 °C, triethylchlorogermane (0.15 g, 0.75 mmol). After 15 mn, the mixture was allowed to warm up to 40 °C for 1 h. Then, THF was replaced by benzene and lithium chloride separated by centrifugation. Evaporation of the solution under vacuo gave 0.34 g of a white powder of **3** (yield 73 %). MP: 117–119 °C. ^{1}H NMR ($CDCl_3$): δ 2.22 (s, 27H, pCH_3+oCH_3); 6.77 (s, 6H, C_6H_2); 0.73–1.04 (m, 15H, Et_3Ge). ^{13}C NMR ($CDCl_3$): δ 21.02 (pCH_3); 23.92 (oCH_3); 136.82 (C_1); 143.38 (C_2); 129.39 (C_3); 138.59 (C_4); 8.05 (CH_2, ethyl); 7.86 (CH_3, ethyl). IR ($CDCl_3$): 2135 cm^{-1} (NCN). MS (EI, m/z, %): 630, 5% (M^{+}.); 601, 42% (M^{+}.-ethyl); 543, 16% (M^{+}.-3 ethyl); 511, 10% (M^{+}.-Mes).

Thermal decomposition of 3

A solution of **3** (0.05 g, 0.08 mmol) in 0.5 mL of $CDCl_3$was heated at 100 °C. The decomposition is followed by ^{1}H NMR. After 3 days, formations of **1** and $Et_3GeNCNGeEt_3$[6] are quantitative.

Action of t-Buli on $Et_3GeNCNGeEt_3$, followed

By addition of Et_3GeCl

To $Et_3GeNCNGeEt_3$ (0.47 g, 1.30 mmol) in 3 mL of THF, was added t-BuLi (1.7 M in pentane), (0.76 mL, 1.30 mmol). Et_3GetBu was identified in gaz chromatography (79 %, dosage GC, reference Et_4Ge) and GC/mass spectrometry by comparison to a pure sample prepared by stoechiometric addition of Et_3GeCl on t-BuLi. Addition of Et_3GeCl (0.25 g, 1.30 mmol) on the reactional mixture, leads to quantitative formation of $Et_3GeNCNGeEt_3$(conform to litterature[2,6]) besides Et_3GetBu.

By addition of Me_3SiCl

As before, reaction between $Et_3GeNCNGeEt_3$ (0.30 g, 0.85 mmol) and t-BuLi (1.7 M in pentane) (0.50 mL, 0.85 mmol) was followed by addition of Me_3SiCl (0.09 g, 0.85 mmol). GC/mass and ^1H NMR analysis showed the formation of Et_3GetBu, $Me_3SiNCNSiMe_3$ (18%) and $Et_3GeNCNSiMe_3$ (**4**) (conform to litterature[9]) (82%).

Preparation of $Mes_3GeNCNGeClEt_2$ (5)

To Et_2GeCl_2 (0.10 g, 0.5 mmol) in 2 mL of THF was added dropwise under stirring at -65 °C, $Mes_3GeNCNLi$ (0.5 mmol) in 5 mL of THF. The mixture was allowed to warm to -25 °C. After 2 h at −25 °C, THF was replaced by ether and lithium chloride separated by centrifugation. The remaining solution, concentrated under vacuo, led to 0.27 g of a white powder of **5** (yield 87 %). MP: 114–116 °C. ^1H NMR ($CDCl_3$): δ 2.24 (s, 27H, pCH_3+oCH_3); 6.81 (s, 6H, C_6H_2); 1.14–1.17 (m, 10H, Et_2GeCl). ^{13}C NMR ($CDCl_3$): δ 21.05 (pCH_3); 24.48 (oCH_3); 136.94 (C_1); 143.34 (C_2); 129.79 (C_3); 139.43 (C_4); 12.30 (CH_2, ethyl); 7.27 (CH_3, ethyl). IR ($CDCl_3$): 2140 cm^{-1} (NCN). MS (EI, m/z,%): 636, 2% (M^+.); 517, 12% (M^+.-Mes); 482, 12% (M^+.-Mes-Cl); 459, 100% (M^+.-Mes-2Et).

Preparation of $Mes_3GeNCNGeEt_2NCNGeEt_2NCNGeMes_3$ (6)

To $Mes_3GeNCNGeClEt_2$ **5** (0.41 g, 0.64 mmol) in 6 mL of THF was added dropwise under stirring at room temperature dilithium cyanamide (0.32 mmol) in 3 mL of THF. After 1.5h at 50 °C, the mixture was allowed to warm to room temperature. THF was replaced by benzene and lithium chloride separated by centrifugation. The remaining solvent evaporated under vacuo led to 0.27 g of **6** as a yellow sticky compound (yield 69 %). ^1H NMR ($CDCl_3$): δ 2.19 (s, 36H, oCH_3); 2.23 (s, 18H, pCH_3); 6.76 (s, 12H, C_6H_2); 1.16–0.82 (m, 20H, Et_2Ge). ^{13}C NMR ($CDCl_3$): δ 21.04 (pCH_3); 23.88 (oCH_3); 136.38 (C_1); 143.40 (C_2); 129.44 (C_3); 138.70 (C_4); 12.32 (CH_2, ethyl); 12.69 (CH_2, ethyl); 7.36 (CH_3, ethyl); 7.29 (CH_3, ethyl). IR ($CDCl_3$): 2188–2055 cm^{-1} (NCN). MS (DCI/CH_4, m/z,%): 1243, 16% $(M+1)^+$; 1123, 2% $(M\text{-}Mes)^+$.

Preparation of $Mes_3GeNCNGeEt_2NCNGeMes_3$ (7)

To $Mes_3GeNCNLi$ (1.00 mmol) in 9 mL of THF, Et_2GeCl_2 (0.10 g, 0.50 mmol) was added dropwise under stirring at –60 °C, the mixture was allowed to warm to room temperature for 17 h. Then, THF was replaced by benzene and lithium chloride separated by centrifugation. Evaporation of the solvent under vacuo led to 0.39 g of a white powder of **7**, recrystallised in ether (yield 72 %). MP: 197–198 °C. ^1H NMR ($CDCl_3$): δ 2.17 (s, 36H, oCH_3); 2.22 (s, 18H, pCH_3); 6.74 (s, 12H, C_6H_2); 0.83–0.81 (m, 10H, Et_2Ge). ^{13}C NMR ($CDCl_3$): δ 21.02 (pCH_3); 23.86 (oCH_3); 136.39 (C_1); 143.40 (C_2); 129.43 (C_3); 138.69 (C_4); 11.69 (CH_2, ethyl); 7.34 (CH_3, ethyl). IR ($CDCl_3$): 2119 cm^{-1} (s), 2171 cm^{-1}(NCN); (in KBr): 2119 and 2155 cm^{-1} (NCN). MS (DCI/CH_4, m/z,%): 1071, 27% $(M+1)^+$; 1099, 6% $(M+29)^+$.

Molecular modelisation for 7

Selected bond lengths and angles for the most stable conformer of **7** in molecular modelisation (program Biosym, Insight II, $Discover_3$, ESFF force field) are given table II.

TABLE II Molecular modelisaton: selected bond lengths (Å) and angles (°) for **7**

Ge1N1	1.88	N1C1N2	178.56
Ge2N3	1.88	N3C2N4	179.51
Ge3N2	1.87	Ge1N1C1	135.09
Ge3N4	1.87	Ge2N3C2	135.65
N1C1	1.30	Ge3N4C2	135.57
C1N2	1.30	Ge3N2C1	136.00
N3C2	1.30	N2Ge3C3	111.68
C2N4	1.30	N2Ge3C5	108.79
		N2Ge3N4	107.59
		C5Ge3C3	109.74
		C5Ge3N4	108.73
		C3Ge3N4	110.24

X-ray analysis of 7

$C_{60}H_{76}Ge_3N_4$, M = 1071.02, triclinic, P $\bar{1}$, a = 12.480(2) Å, b = 12.895(2) Å, c = 17.636(2) Å, α = 80.22(2)°, β = 85.74(2)°,

$\gamma = 77.45(1)°$, $V = 2728.0(7)$ Å^3, Z = 2, ρ_c 1.304 Mg m^{-3}, $F(000) = 1120$, $\lambda = 0.71073$ Å, T = 173(2) K, μ (Mo Kα) = 1.683 mm^{-1}, crystal size 0.8 × 0.7 × 0.2 mm, 2.64° < Θ < 26.37°, 28501 reflections (10374 independent, $R_{int} = 0.0701$) were collected at low temperatures using an oil-coated shock-cooled crystal[15]on a STOE-IPDS diffractometer. The structure was solved by direct methods (SHELXS-97)[16] and 46 parameters using 25 restraints were refined using the least-squares method on F^2 [17]. Largest electron density residue: 1.383 e Å^{-3}, R_1 (for $F>2\sigma(F)$) = 0.049 and $wR_2 = 0.138$ (all data) with $R_1 = \Sigma\|F_o| - |F_c\|/\Sigma|F_o|$ and $wR_2 = (\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2)^{0.5}$. A desorder of the methyl groups of the ethyl substituents were refined anisotropicaly using ADP and distances restraints. The occupancies were refined to 86/14 and 90/10 respectively. Crystallographic data (excluding structure factors) for the structure of **7** have been deposited with the Cambridge Crystallographic Data center as supplementary publication n° CCDC-128882. Copies of the data can be obtained free of charge on application to CCDC, 12 Union road, Cambridge CB21EZ, UK (fax(+44)1223–336–033; e-mail: deposit@ccdc.cam.ac.uk).

Preparation of $(Mes_3GeNCN)_2SbMes$ (8)

To $Mes_3GeNCNLi$ (0.64 mmol) in 7 mL of THF, $MesSbCl_2$(0.10 g, 0.32 mmol) was added dropwise under stirring at –65 °C. After 10 mn at –65 °C, the mixture was allowed to warm to room temperature. After 17 h, THF was replaced by benzene and lithium chloride separated by centrifugation. Concentration of the solution under vacuo yielded 0.29 g of a white powder of **8** (yield 76 %). MP: 119–122 °C (with decomposition). ^1H NMR ($CDCl_3$): δ 2.20 (s, 63 H, oCH_3+ pCH_3, Mes_3Ge+MesSb); 6.72 (s, 14 H, C_6H_2, Mes_3Ge+MesSb). ^{13}C NMR ($CDCl_3$): δ: Mes_3Ge: 21.04 (pCH_3); 23.97 (oCH_3); 138.65 (C1); 143.67 (C2); 129.42 (C3); 137.42 (C4); MesSb: 21.04 (pCH_3); 23.73 (oCH_3); 138.39 (C′1); 143.30 (C′2); 130.09 (C′3); 139.13 (C′4); 136.39 (NCN). IR ($CDCl_3$): 2135 cm^{-1} (NCN). MS (DCi/CH_4, m/z, %): 1081, 17% $(M+1)^+$.

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