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Note

Poly(germaniumpolycarbodiimides)

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Abstract

Poly(metalpolycarbodiimides) were obtained from cyanamide or dilithium cyanamide and di-, tri- or tetra-chlorogermanes by dehydrochlorination, transmetallation or exchange GeCl/GeN reactions. The preparation was extended to mesityldichlorostibane. Metal polyhalides develop a high tendency to generate poly(metalcarbodiimide) cryptands in spite of the linear molecular shape of the carbodiimide links. In these oligomeric structures, the reactivity of the metal nitrogen bond towards protic reagents is preserved and allows the confirmation of their structure by chemical investigations.

Keywords: Germylpolycarbodiimides; Mesitylstibylcarbodiimide; Poly(metalpolycarbodiimide); Methoxygermane; Spirogermanes; Metalcarbodiimide cryptands

1. Introduction

Following the extensive use of calcium carbodiimide during the years 1925–1962 [1], the metalcyanamide chemistry was developed, including alkaline metal, alkaline earth metal, transition metals [2,3], rare earth metals, [1] and main group 14 elements [4] and Boron [5].

In the particular case of group 14 elements, the metallated carbodiimides were prepared from metathesis reactions [6]: (i) between a metal halide and a metallated carbodiimide (Eqs. (1) and (2)) or (ii) between the same metal halide and cyanamide in the presence of a basic amine (Eq. (3))

$$2R_3SiCl + Ag_2NCN \rightarrow 2AgCN + R_3Si\text{-}NCN\text{-}SiR_3 \quad (1)$$

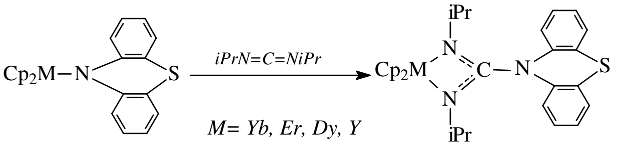
$$RCl_2Si\text{-}SiCl_2R + Me_3Si\text{-}NCN\text{-}SiMe_3 \rightarrow 2Me_3SiCl + 1/n[\text{-}Me_2Si\text{-}SiMe_2\text{-}NCN\text{-}]n \quad (2)$$

$$2R_3SiCl + H_2NCN + 2C_5H_5N \rightarrow 2C_5H_5N, HCl + R_3Si\text{-}NCN\text{-}SiR_3 \quad (3)$$

These reactions (Eqs. (1)–(3)) were extended to other metal halides and pseudo halides (Eq. (4)) [7].

$$2Me_3Sn\text{-}NCN^{-}R' + R_2TiCl_2 \rightarrow 2Me_3SnCl + R_2Ti(NCNR')_2 \quad (4)$$

It was shown that the dimetallated carbodiimide form was more stable than the cyanamide form [5,8,9] The carbodimide form was largely investigated by IR [10,11], theoretical studies [12–14] and the activation barrier for the racemization of optically active carbodiimide was evaluated [15,16]. Other metallated carbodiimides were obtained from the insertion of cyanamide or dialkylcarbodiimide into metal nitrogen or metal carbon bonds [7,17–25]. These last reactions often give nitrogenated heterocycles highly delocalized [25] (Eq. (5))



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Over the last decade, these studies of carbodiimide derivatives have played a very important role in a wide array of chemical application, including prebiotic chemistry from interstellar cyanamide [26–29], pure organic chemistry as the relevant transformation of carbon dioxide into symmetrical arylcarbodiimide [30], heterocyclisation [31,32], combinational chemistry [33] and recently materials presenting a high intramolecular electron transfer or magnetic properties [5,6,34], cyclooligomers [5], polymers and carbodiimides latex [35–41]. In this context, we synthesized and studied various germylsubstituted carbodiimides [8,9,42–45]. In the case of cyclic oligomers obtained from the reaction of dimesityldichlorogermane and the dilithium carbodiimide [42], it was found that the trimer $(Mes_2GeNCN)_3$ was always the main product formed. Changing the reaction conditions, it has been possible to isolate the corresponding tetramer and other higher oligomers $(Mes_2GeNCN)_n$ with n up to 20–30.

The aim of this work was on the one hand, to check this tendency of germanium halide and other metal halides to generate metal carbodiimide cryptands in the case of an increase of the number of carbodiimide functions around the metal and on the other hand to study the reactivity of the germanium nitrogen bond in the poly(germanium-polycarbodiimide) towards protic reagents.

2. Experimental

All reactions were carried out under nitrogen and in dry solvents using standard Schlenk tubes techniques. ^1H NMR spectra were recorded on Bruker AC80 (80.13 MHz) and Brucker AC250 (^1H(δ ppm/TMS) instruments); ^{13}C NMR spectra were recorded on Bruker AC200 (50.32 MHz) and ARX 400 (100.62 MHz), (δ ppm/TMS) instruments; Gas Chromatography (GC) was undertaken on a Hewlett-Packard HP 6890 instrument; mass and gas chromatography (GC/mass) and mass spectra were recorded with a Hewlett-Packard HP5989 in electron impact mode (Ei, 70 Ev) or a Nermag R10-10 spectrometer operating in Ei mode or by chemical desorption (DCi/CH_4 or NH_3), or by FAB(N-POE); IR spectra on a Perkin Elmer 1600FT IR spectrometer. Elemental analyses were performed by the "Service Central de Microanalyse" of "Ecole Nationale Supérieure de Chimie de Toulouse". For crystallized compounds, melting points were measured on a Leitz microscope.

2.1. Preparation of $(Et_2GeNCN)_3$ (**1**)

2.1.1. Through dehydrochlorination reaction

Diethyldichlorogermane Et_2GeCl_2 [46] (0.49 g, 2.42 mmol) was added under stirring to a solution of cyanamide (0.10 g, 2.40 mmol) and Et_3N (0.72 g, 7.13 mmol) in 7 mL of THF. The reaction occurs immediately with precipitation of Et_3N, HCl which was filtered after 3 more hours at room temperature. The solution analyzed by GC/mass showed compound **1** ($M^{+\cdot} = 512$) with only traces of Et_2GeCl_2($M^{+\cdot} = 202$). The concentration of the solution under 30 mmHg led to a viscous liquid identified to almost pure compound **1**. Yield 60%.

2.1.2. Using transmetallation reaction

Et_2GeCl_2 (0.36 g, 1.78 mmol) was added under stirring to a suspension of LiNCNLi (1.78 mmol) prepared from H_2NCN (0.075 g, 1.78 mmol) and nBuLi (1.6 M in hexane, 2.22 mL, 3.56 mmol) in 4 mL of THF. After 2 h at room temperature, the THF was replaced by 8 mL of pentane and LiCl was filtered. Concentration of the solution under 30 mmHg gave a viscous liquid which was identified to almost pure (but not distillable without partial decomposition) compound **1**. Yield 65%.

b.p.: 163 °C/30 mmHg ^1H NMR ($CDCl_3$, ppm): δ 1.03–1.10 (m, *Et)*; ^{13}C NMR ($CDCl_3$, ppm): δ 7.22, 7.33 (CH_3^{Et}); 11.62, 12.21 (CH_2^{Et}); 136.41 (NCN). IR (KBr) ν_{as}NCN: 2060 cm^{-1}. Mass (Ei/CH_4): m/z 512 ($M^{+\cdot}$, 6%), 483 ($M^{+\cdot} - Et$, 100%), 454 ($M^{+\cdot} - 2Et$, 11%), 425($M^{+\cdot} - 3Et$, 6%).

2.2. Preparation of $[(MesGe)_2(NCN)_3]_3$ (**2**)

2.2.1. Through dehydrochlorination reaction

The triethylamine (0.72 g, 7.13 mmol) was added at room temperature under stirring to a solution of mesityltrichlorogermane $MesGeCl_3$ [47] (0.71 g, 2.38 mmol) and H_2NCN (0.15 g, 3.57 mmol) in 5 mL of THF. After 3 h at room temperature, THF was replaced with benzene (6 mL) and Et_3N, HCl was filtered. Concentration of the remaining solution under vacuum led to a white powder which was washed with 2 mL of pentane to eliminate possible traces of remaining $MesGeCl_3$. Then compound **2** was dried under vacuum leading to 0.28 g of pure compound. Yield 75%.

m.p.: 147–149 °C. ^1H NMR ($CDCl_3$, ppm): δ 2.22 (s, 3H, p-CH_3); 2.30 (s, 6H, o-CH_3); 6.76 (s, 2H, C_6H_2). ^1H NMR ($CDCl_3$, ppm) δ : 21.20 (p-CH_3); 23.10 (o-CH_3); Mes: 134.67 (C1); 143.80 (C2), 129.67 (C3), 142.13 (C4). IR ($CDCl_3$) ν_{as}NCN: 2138 cm^{-1}. Mass (DCi/CH_4): m/z 1511 (MH^+). *Anal.* Calc. for $C_{63}H_{66}Ge_6N_{18}$: C, 50.08; H, 4.40; N, 16.79. Found: C, 51.17; H, 4.73; N, 16.37%.

2.2.2. Using transmetallation reaction

$MesGeCl_3$ (0.70 g, 2.38 mmol) was added under stirring and at room temperature to a solution of LiNCNLi (3.57 mmol) prepared from H_2NCN (0.15 g, 3.57 mmol) and nBuLi (1.6 M in hexane, 4.46 mL, 7.14 mmol) in 8 mL of THF. After 3 h, THF was replaced by 8 mL of benzene and LiCl was eliminated by filtration. Concentration of the remaining solution under vacuum led to a white powder which was washed with 3 mL of pentane to eliminate possible traces of remaining $MesGeCl_3$. Then compound **2** was dried under vacuum leading to 0.31 g of pure compound. Yield: 84%.

2.3. Preparation of *($MesSbNCN)_5$* (**3**)

A solution of $MesSbCl_2$ [48–50] (0.67 g, 2.14 mmol) in 6 mL of THF was added to a suspension of LiNCNLi (2.14 mmol) prepared from H_2NCN (0.09 g, 2.14 mmol) and *n*BuLi (1.6 M in hexane, 2.68 mL, 4.28 mmol) in 4 mL of THF. After 4 h under stirring at room temperature, the THF was replaced by 5 mL of C_6H_6 and LiCl was filtered. Concentration of the solution under vacuum led to 0.41 g of **3** as a white powder which was then recrystallized in CH_2Cl_2/pentane. Yield: 68%.

m.p.: 155–157°C. ^1H NMR ($CDCl_3$, ppm): δ 2.21 (s, 15H, *p*-CH_3); 2.32 (s, 30H, *o*-CH_3); 6.78 (s, 10H, C_6H_2). ^{13}C NMR ($CDCl_3$, ppm) δ: 21.04 (*p*-CH_3); 23.96 (*o*-CH_3); Mes: 140.25 (C1); 143.70 (C2), 129.22 (C3), 138.74 (C4), 138.36 (NCN). IR ($CDCl_3$) ν_{as}(NCN): 2055 cm^{-1}. Mass (DCi/CH_4): *m/z* 1405 (MH^+). *Anal.* Calc. for $C_{50}H_{55}Sb_5N_{10}$: C, 42.75; H, 3.95; N, 9.97. Found: C, 41.93; H, 4.08; N, 10.18%.

2.4. Preparation of *$[Ge(NCN)_2]_n$* (**4**)

2.4.1. Through dehydrochlorination reaction

To a solution of cyanamide (0.08 g, 1.86 mmol) and Et_3N (0.37 g, 3.72 mmol) in 6 mL of THF, $GeCl_4$ (0.20 g, 0.93 mmol) was added slowly under stirring. After 2 h at room temperature, THF was replaced with 7 mL of $CHCl_3$ to eliminate the soluble Et_3N,HCl. Compound **4** was then isolated by filtration. 0.11 g. Yield: 78%.

2.4.2. Through transmetallation reaction

To a suspension of LiNCNLi (2.86 mmol) prepared from H_2NCN (0.12 g, 2.86 mmol) and nBuLi (1.6 M, 3.57 mL, 5.72 mmol) in 5 mL of THF, $GeCl_4$ (0.30 g, 1.39 mmol) was added at room temperature under stirring. After 3 h, the solution was warmed and LiCl eliminated by filtration. A white powder (0.15 g) of **4** precipitated on cooling and was isolated by filtration. Yield: 71%.

2.4.3. Through GeCl/Ge-N exchange reaction

$GeCl_4$ (0.31 g, 1.43 mmol) was added to a solution of bis(triethylgermyl)carbodiimide [43] (1.03 g, 2.86 mmol) in 3 mL of THF. The exchange reaction was followed by GC from the formation of Et_3 GeCl and until the complete transformation of $(Et_3Ge)_2NCN$. Compound **4** was then isolated by filtration and washed with 3 mL of ether and dried under vacuum (0.16 g). Yield: 73%.

m.p.: >370°C; IR (nujol) ν_{as}(NCN): 2165 cm^{-1}. Mass (FAB, Nitro-Phenyl-Octyl-Ether: NPOE): *m/z* 306 ($M^{+\cdot}$, $[Ge(NCN)_2]_2$), 458 ($M^{+\cdot}$, $[Ge(NCN)_2]_3$). *Anal.* Calc. for $(C_2GeN_4)_n$: C, 15.74; N, 36.71. Found: C, 16.04; N, 36.98%.

2.5. Chemical characterization of **4**

2.5.1. Reaction with methanol

In an NMR tube, were mixed **4** (0.012 g, 0.078 mmol) and a solution of methanol (0.010 g, 0.310 mmol) in 0.5 mL of $CDCl_3$. The insoluble **4** reacted, leading first to a homogeneous solution. Then after 3 h at room temperature, a new white solid precipitated. The analysis of the liquid phase using GC/internal reference and by comparison with an authentic sample of $Ge(OMe)_4$ **5** [51] showed an almost quantitative formation of **5** also characterized by ^1H NMR ($CDCl_3$, δ ppm: 3.66 OCH_3), ^{13}C NMR ($CDCl_3$, δ ppm: 53.44 OCH_3), and mass analysis (Ei): 168 (MH^+ – OMe); 137 (MH^+ – 2MeO); 105 (MH^+ – 3MeO); (DCi/NH_3): 199 (MH^+); 216 ($MNH_4{}^+$); 233 ($MN_2H_7{}^+$). The white precipitate was then identified as cyanamide (m.p.: 46 °C).

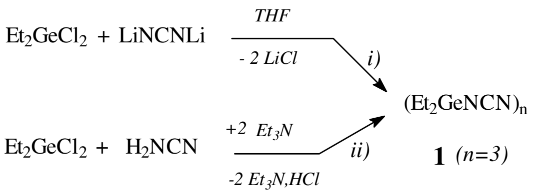
2.5.2. Reaction with 3,5-di-t-butylcatechol

To **4** (0.16 g) in 2 mL of THF was added a solution of 3,5-di-*tert*-butylcathecol (0.46 g, 2.1 mmol) in 5 mL of THF. After 4 h at room temperature and replacement of THF by 4 mL of benzene, the elimination of the insoluble cyanamide by centrifugation led to a solution which, when evaporated under vacuum, gave 0.51 g (yield 94 %) of the spirogermane **6** identified by ^1H NMR [52] ($CDCl_3$/DMSO-d_6, 50/50): 1.23 (s, 18 H, tBu); 1.60 (s, 18H, tBu); 6.68 and 6.85 (m, 4H, C_6H_2) and mass spectroscopy (Ei, *m/z*: $M^{+\cdot}$: 514).

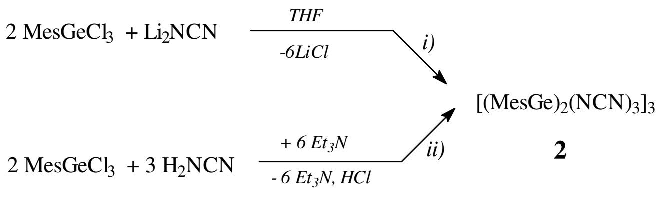
3. Results and discussion

To increase the number of germanium carbodiimide units around the metal, we decided to start from polyhalogenated germanium compounds: Et_2GeCl_2, $MesGeCl_3$ and $GeCl_4$, using their reactions: (i) with the dilithium carbodiimide, (ii)with cyanamide in the presence of a basic amine or (iii) the exchange reaction GeCl/GeN (Schemes 1–3).

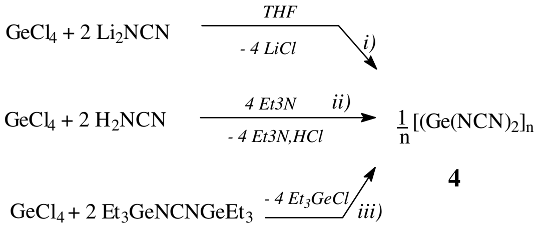
We observed [42] that reaction between dimesityldichlorogermane with dilithium carbodimide gave cyclopoly(dimesithylgermyl carbodiimide) $(Mes_2GeNCN)_n$ with $n = 3$, 4. It was not possible to obtain polymers with higher molecular weight supposedly because the mesityl substituents were quite bulky. Therefore, polygermylcarbodiimide with higher degree of polymerization could be expected using smaller substituents like ethyl groups. The reaction was performed from diethyldichlorogermane



Scheme 1.



Scheme 2.



Scheme 3.

using both (i) and (ii) methods (Scheme 1). However, the only product identified was the cyclic trimer ($n = 3$). Mass analysis showed the molecular ion (Ei) $M^{+\bullet} = 512$. The shape of this molecular ion being characteristic of a Ge_3 molecule.

It seems that, even with smaller substituents, the tendency of the reaction is still the cyclooligomerization.

To increase the number of NCN bond units around germanium, we used $MesGeCl_3$ in reactions (i) and (ii).

Both reactions (i) and (ii) led to similar yields (75–80%) of the same white solid compound. The ^1H and ^{13}C NMR analyses showed only one kind of mesityl signals leading to the conclusion that the reaction gives only one compound which is present in IR as the NCN absorption at 2138 cm^{-1}. The mass spectrometry (DCi/CH_4) analysis allows the characterization of the MH^+ signal at 1511 whose isotopic distribution is typical of a Ge_6 compound confirming the structure $[(MesGe)_2(NCN)_3]_3$.

This crude formula could be attributed mostly to the more stable molecular structure **A** (Fig. 1) from semi empirical calculations performed for $[(MeGe)_2(NCN)_3]_3$ at the Hyperchem PM3 level.

However, as reactions of organogermaniumdi- and trihalides with metalated carbodiimide or cyanamide in the presence of a base (Schemes 1–3) lead mainly to cyclooligomers, we intended to know if this fact can be extended to other metal dihalides and performed reaction (i) with the mesityldichlorostibane (Eq. (6)). The cyclopentamer was characterized in mass spectrometry (DCi/CH_4) by $MH^+ = 1405$ with the isotopic distribution of a Sb_5 compound.

$$MesSbCl_2 + Li_2NCN \xrightarrow[-2LiCl]{THF} \frac{1}{5}\,\underset{\mathbf{3}}{(MesSbNCN)_5} \tag{6}$$

With a metal tetrahalide, the formation of a polydimensional polymer seems to occur.

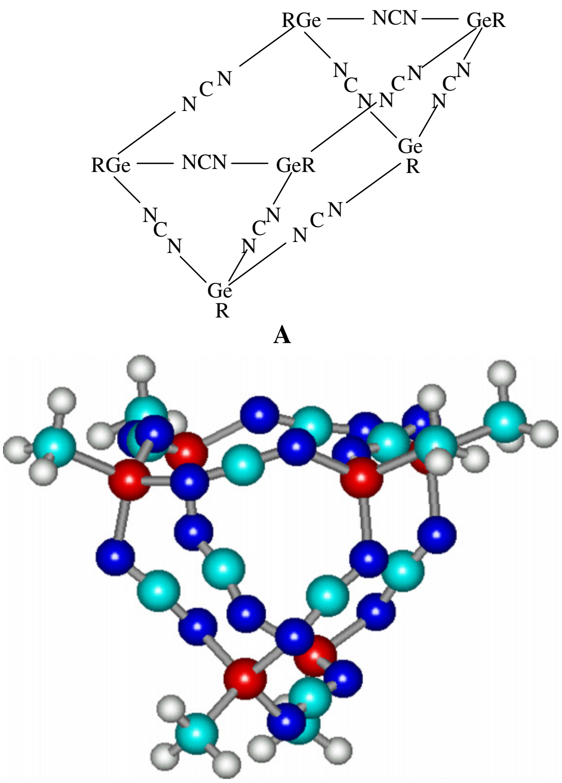


Fig. 1. Proposed formula and geometry optimisation for **A** (R = Me) Hyperchem PM3 level.

Germanium tetrachloride, reacted by the three reactions pathways (i), (ii), (iii), led to the same white solid (Scheme 3).

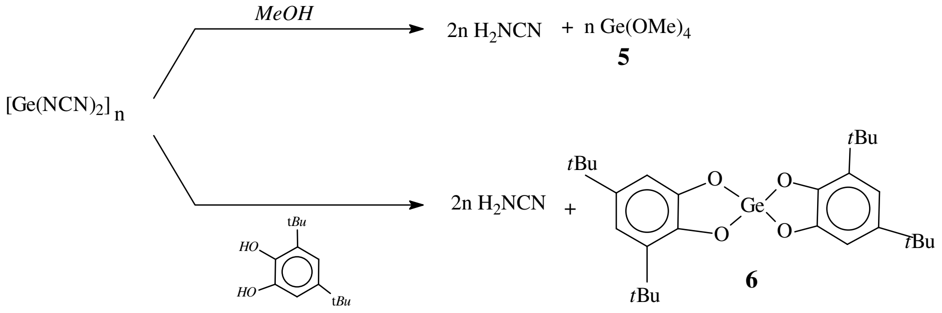
This compound appears physically similar to the compound obtained in the metathesis reaction of germanium tetrachloride with bis(trimethylsilyl)carbodiimide (Eq. (7)) [5]

$$nGeCl_4 + 2nMe_3SiNCNSiMe_3 \rightarrow 4nMe_3SiCl + \underset{\mathbf{4}}{[Ge(NCN)_2]_n} \tag{7}$$

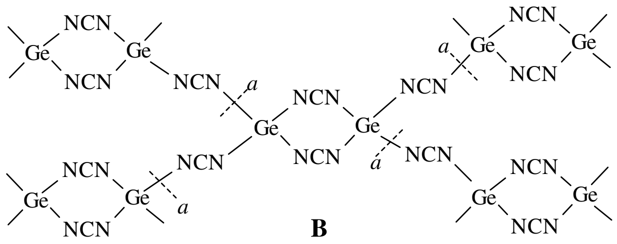
This white solid is insoluble in the classical solvents, which does not allow ^1H and ^{13}C NMR. Infrared analysis shows a characteristic absorption at 2165 cm^{-1} (ν NCN). Mass analysis by FAB (NPOE) technique allows the observation of polymer units ($n = 2$, $M^{+\bullet} = 306$) and ($n = 3$, $M^{+\bullet} = 458$) probably formed from the fragmentation of a polydimensional polymer.

Chemical characterizations using protic cleavages (methanol, 3,5-di-*tert*-butylcatechol) (Scheme 4) of the Ge–N bonds present in the polymer (Scheme 3) confirmed the presence of four germanium nitrogen bonds around the metal.

To explain the observed fragmentation of the $[Ge(NCN)_2]_n$ polymer the most probable hypothesis would be the coexistence in the polymer of polygermacyclic structure of **B** type (Scheme 5) and of polygermaspiranic structure of **C** type (Scheme 6).

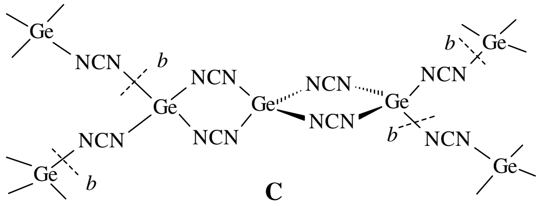


Scheme 4.



a fragmentation leads to $M^{+\cdot} = 306$

Scheme 5.



b fragmentation leads to $M^{+\cdot} = 458$

Scheme 6.

4. Conclusion

Although the carbodiimide function presents a central linear molecular shape, metal polyhalides develop high tendency to generate poly (metalcarbodiimide) cryptands. In these oligomeric structures, the reactivity of the metal nitrogen bond towards protic reagents is preserved and allows the confirmation of their structure by chemical investigations.

Acknowledgements

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