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Journal of Organometallic Chemistry 562 (1998) 191–195

Synthesis and X-ray crystal structure of bis(germyl)carbodiimides. Spectroscopic characterization of (hydrogeno)(germyl)cyanamides

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Received 17 December 1997

Abstract

Bis(triethylgermyl)- and bis(trimesitylgermyl)-carbodiimides are easily formed either by transmetallation or transamination reactions. (Hydrogeno)triethyl- or trimesitylgermyl-cyanamides are characterized in the dehydrohalogenation reaction between cyanamide and triethyl- or trimesityl-chlorogermanes. According to a single X-ray diffraction analysis, bis(trimesitylgermyl)carbodiimide is monomeric and the GeNCNGe framework is not linear, in contrast to tin and silicon analogues, respectively. © 1998 Elsevier Science S.A. All rights reserved.

Keywords: Carbodiimide; Cyanamide; Germanium

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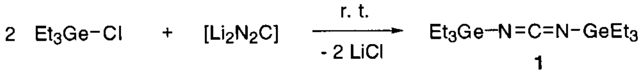
1. Introduction

In the last few years, the chemistry of Group 14 substituted cyanamides and carbodiimides has been significantly developed, mainly because of their potential applications [1–10]. Although (hydrogeno)(stannyl)cyanamides $R_3Sn{-}NH{-}CN$ are known [1,11–14], silyl [1,15] and germyl analogues [16] have never been obtained, probably because of their lack of stability. Our interest in the preparation of new germylated polymers has led us to investigate the possibility of preparing stable $R_3Ge{-}NH{-}CN$ derivatives, and also to find the easiest way to synthesize bis(germyl)carbodiimides. Here we report our results in the triethylgermyl and trimesitylgermyl series.

2. Results and discussion

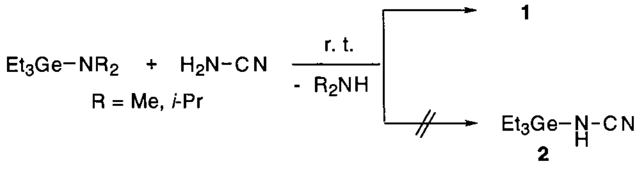
It has been reported that halogermanes react with lead or silver cyanamides affording bis(germyl)carbodiimides [1,17]; not surprisingly addition of triethylchlorogermane to the bis(lithium) salt of cyanamide affords the carbodiimide **1** (Scheme 1).

It is also known that *N*-triethylgermyl–diethylamine reacts with dicyanamide at high temperature (110–200 °C) yielding carbodiimide **1** [1]. Using cyanamide, in-



$$2\ Et_3Ge{-}Cl + [Li_2N_2C] \xrightarrow[-2\ LiCl]{r.t.} \underset{\mathbf{1}}{Et_3Ge{-}N{=}C{=}N{-}GeEt_3}$$

Scheme 1.



Scheme 2.

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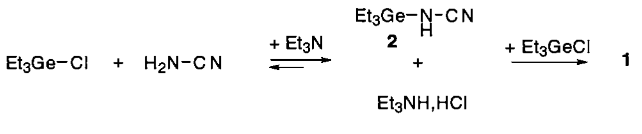
PII S0022-328X(98)00546-4

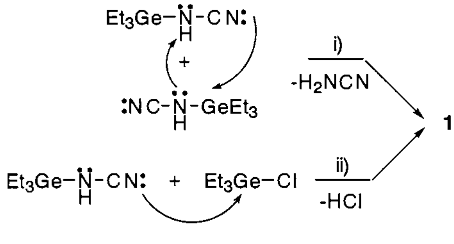


Scheme 3.

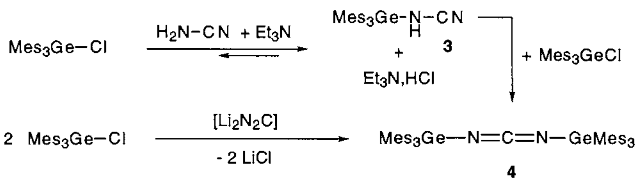
stead of its dimer, the transamination reaction occurs at room temperature (r.t.), quantitatively affording **1**. In the hope of preparing the desired (hydrogeno) (germyl)cyanamide **2**, the sterically hindered *N*-triethylgermyl–diisopropylamine was used (Scheme 2). However, once again, whatever the ratio of the reagents used, carbodiimide **1** was obtained; in the case of the 1/1 ratio, half of the starting cyanamide was recovered unchanged. Note that at the beginning of the sixties [18,19], there was controversy about the structure of bis-metallated NCN compounds of group 14 [cyanamide $(R_3Ge)_2N{-}CN$ versus carbodiimide $R_3Ge{-}NCN{-}GeR_3$]. It is now well established that, in solution, all of them have the carbodiimide structure [1,4,6,7]; the bulky metal groups cannot be accommodated by the same nitrogen atom [7].

Interestingly, when the reaction of triethylchlorogermane with cyanamide, in the presence of triethylamine, was monitored by spectroscopy, the (hydrogeno) (triethylgermyl)cyanamide **2** was detected (Scheme 3). The structure of **2** was clearly established by GC/mass spectrometry [203: $(M+1)^+$], infrared [3381 (NH), 2193 (CN) cm^{-1}] and ^{13}C-NMR spectroscopy (117 ppm: CN). Without further treatment, the reaction mixture eventually leads to **1**.

We obtained evidence that the formation of **2** is limited by the reverse cleavage reaction of the Ge–N bond by the triethylammonium chloride, acting as a protic species. Indeed, the yield of **2** increased when an excess of cyanamide was used (ratio 1:6), or by removing the ammonium salt from the reaction mixture by precipitation and filtration. We also observed that the excess of cyanamide in THF solution prevents the transformation of **2** into **1**, so does nitromethane and, slightly less efficiently, acetonitrile (cf. Section 4, Tables 3 and 4). Two competitive mechanisms (Scheme 4) can rationalize the formation of **1** from **2**: (i) a disproportionation of **2** giving back cyanamide along with **1**; (ii) the reaction of **2** with the triethylchlorogermane which is present in the reaction mixture.



Scheme 4.



Scheme 5.

Since neither nitromethane nor acetonitrile prevented the transamination reaction between triethylgermylamine and cyanamide (Scheme 2), in which **2** is almost certainly the intermediate, it is quite likely that these solvents strongly complex triethylchlorogermane, thus preventing any nucleophilic attack. A further support for this hypothesis was found in the fact that no reaction occurred when reacting triethylchlorogermane with cyanamide and triethylamine in nitromethane.

In the hope of isolating a (hydrogeno)(germyl)cyanamide, trimesitylchlorogermane was used as the electrophile. However, a mixture of germylcyanamide **3** and bis(germyl)carbodiimide **4** was obtained. Attempts to isolate **3** by recrystallization from a nitromethane solution, which prevents the formation of **4**, failed. Of course, the bis(trimesitylgermyl)carbodiimide **4** was the only final product when trimesitylchlorogermane was added to the bis(lithium) salt of cyanamide (Scheme 5).

Since the solid state structure of bis(trimethylstannyl)carbodiimide [20] and bis(triphenylsilyl)carbodiimide [21] are known and are quite different, it was of interest to carry out a single X-ray diffraction study of the bis(germyl)carbodiimide **4**. In the solid state, the structure of the bis(trimethylstannyl)carbodiimide consists of an infinite helical network of planar trimethyltin groups linked by linear NCN units with SnNC angles of 117.6°; all nitrogen atoms are coordinated to two tin units with crystallographically identical tin–nitrogen bonds (2.47 Å). In other words, tin atoms are midway between two NCN fragments, which can be seen as carbodiimides or alternatively as cyanamides (NC: 1.24 Å). In contrast, the bis(triphenylsilyl)carbodiimide is monomeric with a perfectly linear SiNCNSi unit and short SiN (1.70 Å) and CN (1.16 Å) bond lengths. These results are consistent with delocalization of nitrogen lone pairs into the SiC σ^*-orbitals, and with the interaction of the NC antibonding π-orbitals with the SiC σ-orbitals. The results of the X-ray diffraction analysis of **4** are shown in Fig. 1, Tables 1 and 2. Compound **4** is monomeric, the NCN fragment is nearly linear [176.0(3)°], but in contrast with the silicon case, the germanium atoms are out of this chain [GeNC: 154.9(2) and 143.3(2)°]. As discussed in the gas phase study of germyl pseudohalides [22], the GeNC angles do not provide evidence for the back donation from the NCN fragment to the germanium atoms, but the GeN [1.832(2) and 1.836(2) Å] and the NC bond lengths [1.199(3) and 1.206(3)Å] do. Lastly, probably because of the bulky mesityl groups, there is a GeNNGe dihedral angle of 126.5(3)°.

The influence of solvents on the stability and formation of **2** is shown in Tables 3 and 4.

3. Conclusion

To our knowledge [16], (triethylgermyl)- and (trimesitylgermyl)-cyanamide **2** and **3**, although not isolated as pure samples, are the first examples of hydrogenocyanamide ever characterized in the germanium series. Carbodiimide **4** is monomeric in the solid state, in contrast to tin analogues, and the GeNCNGe framework is not linear, in contrast to the silicon analogues. The use of these air-stable germylcarbodiimides as precursors for inorganic polymers is under active investigation.

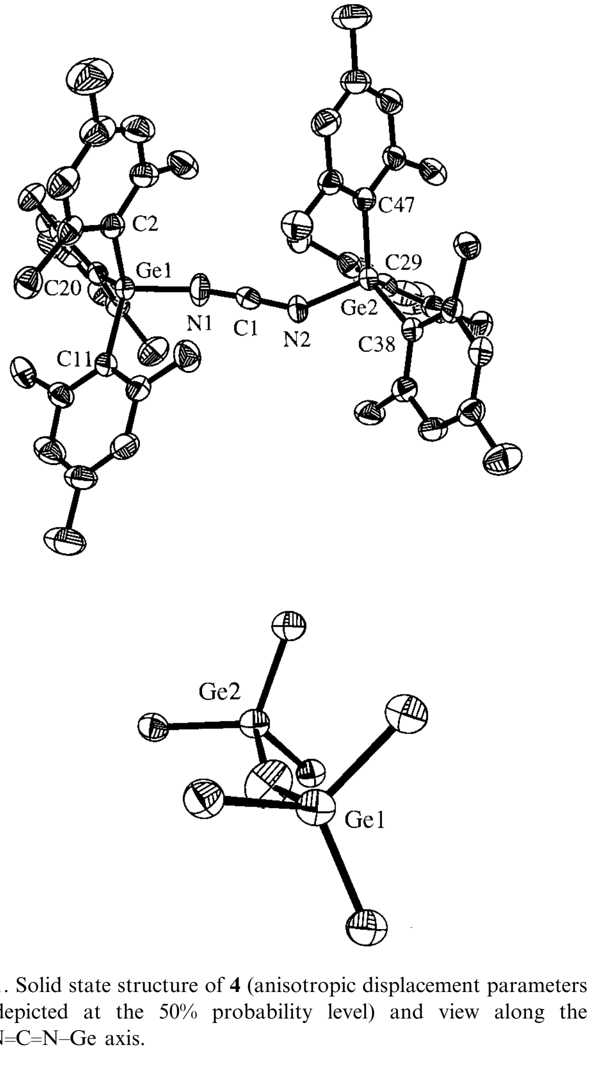


Fig. 1. Solid state structure of **4** (anisotropic displacement parameters are depicted at the 50% probability level) and view along the Ge–N=C=N–Ge axis.

Table 1
Crystallographic data for 4

Formula	$C_{55}H_{66}Ge_2N_2$
Formula mass	900.28
Color	Colorless
Crystal size (mm)	0.8 × 0.7 × 0.4
Temperature (K)	193(2)
$F(000)$	948
Crystal system	Triclinic
Space group	$P\bar{1}$
a [Å]	13.294(3)
b [Å]	13.509(3)
c [Å]	15.356(3)
α [°]	101.39(3)
β [°]	110.15(3)
γ [°]	100.78(3)
V [Å^3]	2438.6(9)
Z	2
ρ_{calcd} [mg cm^3]	1.226
μ [mm^{-1}]	1.269
Max./min. peaks in final difference map (e Å^{-3})	0.500; −0.405
R_1 ($I>2\sigma(I)$)	0.0321
wR_2 (all data)	0.0853
Goodness-of-fit on F^2	1.002

4. Experimental section

All reactions were performed in dry solvents, under dry nitrogen using standard Schlenk techniques. The compounds where characterized by usual analytical techniques: δ ppm, ^{1}H-NMR, AC 80 Bruker; ^{13}C-NMR AC 200; IR: Perkin Elmer 1600 FT; mass spectra, Ribermag R1010 (DCI, CH_4) and HP 5989 (EI). Gas chromatography: Hewlett Packard 6890 GC (column HP1, methylsilicon).

Table 2
Selected bond length (Å) and angles (°) for 4.

Ge(1)–N(1)	1.832(2)	Ge(1)–C(2)	1.9 63(3)
Ge(1)–C(20)	1.975(2)	Ge(1)–C(11)	1.978(3)
Ge(2)–N(2)	1.836(2)	Ge(2)–C(38)	1.969(2)
Ge(2)–C(47)	1.976(3)	Ge(2)–C(29)	1.977(3)
N(1)–C(1)	1.199(3)	C(1)–N(2)	1.206(3)
C(2)–C(7)	1.407(4)	C(2)–C(3)	1.418(4)
N(1)–Ge(1)–C(2)	105.7(1)	N(1)–Ge(1)–C(20)	100.5(1)
C(2)–Ge(1)–C(20)	115.0(1)	N(1)–Ge(1)–C(11)	105.9(1)
C(2)–Ge(1)–C(11)	113.3(1)	C(20)–Ge(1)–C(11)	114.7(1)
N(2)–Ge(2)–C(38)	100.8(1)	N(2)–Ge(2)–C(47)	108.5(1)
C(38)–Ge(2)–C(47)	114.1(1)	N(2)–Ge(2)–C(29)	103.7(1)
C(38)–Ge(2)–C(29)	115.6(1)	C(47)–Ge(2)–C(29)	112.6(1)
C(1)–N(1)–Ge(1)	154.9(2)	N(1)–C(1)–N(2)	176.0(3)
C(1)–N(2)–Ge(2)	143.2(2)	C(7)–C(2)–C(3)	118.3(2)
C(7)–C(2)–Ge(1)	120.6(2)	C(3)–C(2)–Ge(1)	121.1(2)
C(16)–C(11)–Ge(1)	121.9(2)	C(12)–C(11)–Ge(1)	118.6(2)
C(25)–C(20)–Ge(1)	122.9(2)	C(21)–C(20)–Ge(1)	118.4(2)
C(30)–C(29)–Ge(2)	122.7(2)	C(34)–C(29)–Ge(2)	118.6(2)
C(43)–C(38)–Ge(2)	123.1(2)	C(39)–C(38)–Ge(2)	118.6(2)
C(48)–C(47)–Ge(2)	120.3(2)	C(52)–C(47)–Ge(2)	121.0(2)

Table 3
Influence of nucleophilic solvents on the stability of **2** in the reaction mixture

Solvent	Time	Et_3GeCl%	**2**%	**1**%
	Starting time	67	33	0
$CDCl_3$	20’	33	25	42
	18 h or 3 days	49	0	51
CH_3NO_2	20’	67	33	0
	3 days	67	33	0
CH_3CN	3 days	35	30	35

4.1. *Bis(triethylgermyl)carbodiimide (**1**)*

(a) By transmetallation from lithium cyanamide: To a solution of H_2NCN (1.03 g, 24.5 mmol) in 16 ml of THF was added at −65°C under stirring 49 mmol of *t*-BuLi (28.82 ml, 1.7 M in pentane). The reaction mixture was warmed to r.t. after ca. 30 min. Then Et_3GeCl (9.56 g, 49 mmol) was added under stirring. After LiCl filtration, spectroscopic analyses indicated the quantitative formation of **1**. A distillation (Eb: 162°C/17 mm Hg; in conformity with Refs. 1 and 17) afforded 5.56 g of **1** (63% yield); Mass spectrometry (EI): M^+: 360 (1%), M^+-Et: 331 (100%), M^+-2Et: 302 (15%), M^+-3Et: 273 (10%); IR ($CDCl_3$): 2108 cm^{-1}: (ν_{as} N=C=N); ^{1}H-NMR ($CDCl_3$) δ C_2H_5: 0.85–0.91 (m); ^{13}C-NMR ($CDCl_3$, 25°C): δ 134.44 (NCN), 7.88 (CH_3), 7.46 (CH_2).

(b) By transamination reaction from triethylgermyldimethylamine: To a solution of H_2NCN (0.05 g, 1.19 mmol) in 3 ml of THF (or CH_3NO_2) at 20°C, was added under stirring Et_3GeNMe_2 (0.24 g, 1.19 mmol). The reaction was exothermic with evolution of dimethylamine. According to GC, and ^{1}H- and ^{13}C-NMR spectroscopy, the reaction was quantitative.

(c) By transamination from triethylgermyldiisopropylamine: in a similar way H_2NCN (0.05 g, 1.19 mmol) and $Et_3GeNiPr_2$ (0.21 g, 0.80 mmol) quantitatively led to **1** with elimination of diisopropylamine.

4.2. *Preparation and characterization of (**2**)*

To a THF solution (4 ml) of cyanamide (0.30 g, 7.14 mmol) was added Et_3GeCl (0.23 g, 1.19 mmol). Et_3N (0.120 g, 1.19 mmol) was added to the mixture under stirring at r.t. A precipitation of $Et_3N\cdot HCl$ was observed. After 15 min, GC analysis (Et_4Ge as internal standard) showed $Et_3GeNHCN$ **2** (33%)[1], Et_3GeCl (67%), **1** (0%). After filtration of the triethylammonium chloride and evaporation of the solvent under 30 mm Hg, immediate spectroscopic analysis allowed the characterization of **2**: GC/Mass: $(M+1)^+$: 203 (8%), $(M+1)^+$-Et: 174 (100%); $(M+1)^+$-3Et: 116 (50%); IR ($CDCl_3$): 3381 (NH); 2193 (C$\equiv$N) cm^{-1}; ^{1}H-NMR ($CDCl_3$, 25°C): 0.88 (m, 15H, C_2H_5), 4.1 (s, 1H, NH); ^{13}C-NMR ($CDCl_3$, 25°C): 117.00 (N–C$\equiv$N), 7.87 (CH_3), 7.39 (CH_2).

4.3. *Preparation and characterization of trimesitylgermylcyanamide (**3**)*

Trimesitylgermylcyanamide **3** was prepared in a similar way as **2**, using cyanamide (0.15 g, 3.57 mmol), Mes_3GeCl (0.27 g, 0.59 mmol) and Et_3N (0.06 g, 0.59 mmol). After filtration of $Et_3N\cdot HCl$ and evaporation of the solvent under vacuo, the white residue was analyzed by ^{1}H NMR spectroscopy: Mes_3GeCl (31%), **3** (52%), **4** (17%). Spectroscopic data for **3**: Mass spectrum (DCI, CH_4): $(M\text{-}1)^+$: 471 (6%), $(M\text{-}1)^+$-Mes: 352 (16%); IR($CDCl_3$): 3427 (NH), 2258 (N–C$\equiv$N) cm^{-1}; ^{1}H-NMR (C_6D_6, 25°C): 2.07 (s, 9H, *p*-CH_3), 2.30 (s, 18H, *o*-CH_3), 6.70 (s, 6H, C_6H_2); ^{13}C-NMR ($CDCl_3$, 25°C): 21.04 (*p*-CH_3), 23.91 (*o*-CH_3), 134.70 (C1), 143.25 (C2), 129.86 (C3), 139.68(C4), 114.48 (N–C$\equiv$N).

Derivative **3** in THF, benzene, or $CDCl_3$, was slowly converted at r.t. into **4**, and rapidly when heated for 30

Table 4
Influence of the Et_3GeCl/H_2NCN ratio on the formation of **2**

Starting relative proportions Et_3GeCl/H_2NCN (solvent THF)	Et_3N	CPV analysis (relative percentages) % **2**	% **1**
1/6	3	100	0
1/4	3	34	66
1/1	3	14	86
4/1	3	2	98
6/1	3	0	
1/1	(1) $3Et_3N$ (2) after 15 min, $+5CH_3NO_2$	100	100

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[1] By addition of a chloroform solution of $Et_3N\cdot HCl$, the percentage of **2** decreased while that of Et_3GeCl increased. In contrast, cooling the solution to −35°C, favored the precipitation of $Et_3N\cdot HCl$, and the percentage of **2** increased; **2**: 42%, Et_3GeCl: 58%, **1**: 0% (percentages, measured by GC with Et_4Ge as internal standard).

min at 60°C. In a way similar to that observed for **2**, addition of CH_3NO_2 prevented the transformation of **3** into **4.** All attempts to recrystallize **3** in nitromethane failed. In C_6H_6 or ether, after filtration of excess cyanamide, crystals of **4** were obtained.

*4.4. Synthesis of bis(trimesitylgermyl)carbodiimide (**4**) by transmetallation from lithium cyanamide*

Lithium cyanamide prepared as for **1** [H_2NCN (0.01 g, 0.32 mmol), *t*-BuLi: (0.64 mmol)], was added into a THF solution (3 ml) of Mes_3GeCl (0.30 g, (0.64 mmol)]. The reaction mixture was heated at 55°C for 2 h. THF was replaced by benzene and LiCl eliminated by centrifugation. Evaporation of the solvents under vacuo led to 0.25 g (75% yield) of a white residue identified as **4**; recrystallization from ether afforded colorless crystals; m.p.: 237–238°C; Mass spectrum (DCI, CH_4) $(M+1)^+$: 901 (30%), $(M+1)^+$-CH_4: 885 (12%), $(M+1)^+$-MesH: 781 (18%); IR ($CDCl_3$): 2158; (nujol mull): 2179 (ν_{as} $N=C=N$) cm^{-1}. ^{1}H-NMR ($CDCl_3$, 25°C): 2.08 (s, 36H, *o*-CH_3), 2.23 (s, 18H, *p*-CH_3), 6.70 (s, 12H, C_6H_2); ^{13}C-NMR ($CDCl_3$, 25°C): 21.02 (*p*-CH_3), 23.74 (*o*-CH_3), 137.23 (C1), 143.47 (C2), 129.27 (C3), 138.33 (C4), 136.44 ($N=C=N$).

*4.5. Crystal and X-ray experimental data for (**4**)*

The crystal data for **4** are presented in Table 1. The data were collected on a STOE-IPDS diffractometer with Mo–Kα ($\lambda = 0.71073$ Å) radiation using φ-scans. The structure was solved by direct methods using SHELXS-97 [23] and refined with all data on F^2 with a weighting scheme of $\omega^{-1} = \sigma^2(F_o^2) + (g1 \cdot P)^2 + (g2 \cdot P)$ with $P = (F_o^2 + 2F_c^2)/3$ using SHELXL-97. [24] All non-hydrogen atoms were treated anisotropically.

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