

Hydrogermolysis reactions involving the α -germylated nitriles R_3GeCH_2CN ($R = Ph, Pr^i, Bu^t$) and germanium amides R_3GeNMe_2 ($R = Pr^i, Bu^t$) with Ph_3GeH : Substituent-dependent reactivity and crystal structures of $Pr_3^iGeGePh_3$ and $Bu_3^tGe[NHC(CH_3)CHCN]$

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Abstract

The α -germylated nitriles R_3GeCH_2CN ($R = Ph, Pr^i, Bu^t$) and germanium amides R_3GeNMe_2 ($R = Pr^i$ and Bu^t) have been prepared and characterized and their reactivity with Ph_3GeH in CH_3CN has been explored to investigate their utility for the construction of Ge–Ge bonds. In each case the phenyl and *iso*-propyl derivatives furnish the corresponding digermanes $R_3GeGePh_3$ ($R = Ph, Pr^i$) where the amide reagents are converted to R_3GeCH_2CN *in situ* which subsequently react with Ph_3GeH . The rate of the Ge–C bond cleavage reactions was found to depend on the steric and electronic properties of the organic substituents. Attempted synthesis of $Bu_3^tGeGePh_3$ by these methods did not result in the desired product but rather in isolation of the 3-amidocrotononitrile species $Bu_3^tGe[NHC(CH_3)CHCN]$. The crystal structures of $Pr_3^iGeGePh_3$ and $Bu_3^tGe[NHC(CH_3)CHCN]$ have been determined.
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1. Introduction

The synthesis of heavy group 14 oligomers is of interest due to the optical and electronic properties exhibited by these systems resulting from their inherent σ -delocalization. Well-developed methods for the preparation of silicon- [1–11] and tin- [12–28] containing oligomers and polymers have been known for some time. In the case of germanium, until recently existing methods for the synthesis of oligomeric systems have been complicated by low yields and/or the formation of mixtures of products [29–

56]. Improvements in this regard have been made by the use of SmI_2 to promote Ge–Ge bond formation [57,58], the insertion reactions of germylenes into germane Ge–H bonds [59], and use of the hydrogermolysis reaction for Ge–Ge bond formation [60].

We recently reported on the latter process in which a germanium hydride R_3GeH and a germanium amide R_3GeNMe_2 are used as the starting materials [60]. The hydrogermolysis reaction involving these two reagents only yields the desired products when CH_3CN is employed as the reaction medium and this process was shown to proceed via initial conversion of the amide to an α -germylated nitrile R_3GeCH_2CN by reaction of the amide with the solvent, thus rendering CH_3CN not only a solvent but also a

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reagent in the reaction. The α -germylated nitrile is therefore the active species in this interconversion, and the general lability of the Ge–C bond in reactions $\text{Et}_3\text{GeCH}_2\text{CN}$ with various substrates has been reported [61,62].

We have continued to investigate the utility of α -germylated nitriles as synthons for the construction of Ge–Ge bonds, since these materials can be prepared by a one-pot method [60] from the corresponding chlorides and LiCH_2CN [63]. Specifically, we have attempted the synthesis of three digermanes $\text{R}_3\text{GeGePh}_3$ ($\text{R} = \text{Ph}, \text{Pr}^i, \text{Bu}^t$) from Ph_3GeH and $\text{R}_3\text{GeCH}_2\text{CN}$. During the course of this study, we determined that the phenyl- and *iso*-propyl digermanes could be obtained by this process, but successful Ge–Ge bond formation required longer reaction times than that observed for the preparation of $\text{Bu}_3\text{GeGePh}_3$ [60]. Furthermore, the synthesis of $\text{Bu}_3\text{GeGePh}_3$ could not be achieved using neither the α -germylated nitrile $\text{Bu}_3\text{GeCH}_2\text{CN}$ nor the amide $\text{Bu}_3\text{GeNMe}_2$. However, the latter reaction unexpectedly yielded the 3-amidocrotononitrile species $\text{Bu}_3\text{Ge}[\text{NHC}(\text{CH}_3)\text{CHCN}]$ which was isolated and structurally characterized. These findings are the focus of this paper.

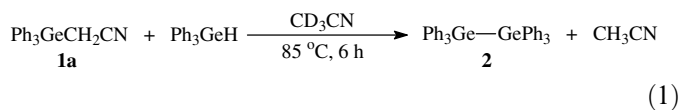
2. Results and discussion

We have shown that the reaction of $\text{Bu}_3\text{GeCH}_2\text{CN}$ with Ph_3GeH generates the digermane $\text{Bu}_3\text{GeGePh}_3$ cleanly in less than 1 h at 85 °C in CH_3CN solvent [60]. Generation of the Ge–Ge bond in this case proceeds much more rapidly than reactions starting with germanium amides R_3GeNMe_2 and germanium hydrides R_3GeH in CH_3CN . The latter process requires a reaction time of 48 h and was shown to proceed by reaction of the amide with CH_3CN to generate the α -germylated nitrile as an intermediate which subsequently reacts with the hydride to furnish the Ge–Ge bond.

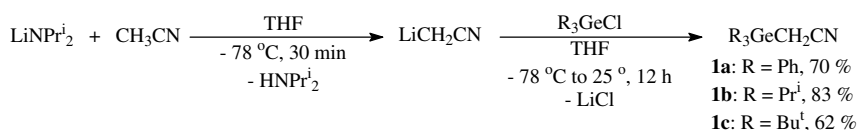
The α -germylated nitriles $\text{Ph}_3\text{GeCH}_2\text{CN}$ (**1a**), $\text{Pr}^i_3\text{GeCH}_2\text{CN}$ (**1b**), $\text{Bu}^t_3\text{GeCH}_2\text{CN}$ (**1c**) were prepared in good to excellent yields from the corresponding monochlorides and LiCH_2CN as shown in Scheme 1. We encountered some difficulty preparing the starting chloride Bu^t_3GeCl used for the synthesis of **1c** by the published procedure involving treatment of GeCl_4 with Bu^tLi [64] which resulted in the generation of oligomeric and polymeric materials from which the desired compound could not be separated. Use of the milder organocuprate $\text{LiCu}(\text{CN})\text{Bu}^t$ as the alkylating agent did furnish the desired product but purification by vacuum distillation required a higher temperature than the published conditions [53].

Compounds **1a–c** were shown to be pure by NMR spectroscopy but we were unable to obtain satisfactory elemental analyses for these materials. These species appear to be thermally unstable but could be isolated and stored at –35 °C in the glovebox for several days. Resonances for the $-\text{CH}_2\text{CN}$ protons were visible in each case in the ^1H NMR spectra of these compounds in C_6D_6 at δ 1.98 (**1a**), 1.43 (**1b**), 1.59 (**1c**) ppm where that for **1a** matches the reported value [61]. The ^{13}C NMR spectra contain resonances for the terminal $-\text{CN}$ groups in the range δ 115–125 ppm and resonances for the α -carbons between δ 20–30 ppm. These values also are similar to those for the structurally characterized compound $[(\text{Me}_3\text{Si})_2\text{CH}]_2\text{Ge}(\text{H})(\text{CH}_2\text{CN})$ [65] although the α -carbon resonances for **1a–c** are shifted downfield relative to that for this species.

The reaction of **1a** with 1 equiv. of Ph_3GeH in CD_3CN solution was monitored by ^1H NMR spectroscopy (Eq. (1)). Compound **1a** exhibits a singlet at δ 2.20 ppm arising from the $-\text{CH}_2\text{CN}$ protons in CD_3CN solution. Upon addition of 1 equiv. of Ph_3GeH to the NMR tube this feature immediately began to decrease in intensity and a new resonance at δ 2.08 ppm began to appear. The singlet at δ 2.08 ppm steadily increased in intensity during the course of the experiment while the intensity of the feature at δ 2.20 ppm decreased. After a total reaction time of 6 h, the downfield singlet was absent while the singlet at δ 2.08 ppm remained, and the feature at δ 5.95 ppm corresponding to Ph_3GeH was also no longer visible. The resonance at δ 2.08 ppm matches exactly with the ^1H NMR feature observed for a sample of CH_3CN in CD_3CN solution which unequivocally indicates the formation of CH_3CN in this process. However, this reaction proceeds slower than that between $\text{Bu}_3\text{GeCH}_2\text{CN}$ and Ph_3GeH which is complete in only 50 min [60]. In order to confirm the generation of $\text{Ph}_3\text{GeGePh}_3$ (**2**), the reaction was carried out on a preparative scale resulting in the isolation of **2** in 88% yield which was characterized by elemental analysis.



Similarly, treatment of **1b** with Ph_3GeH generated the corresponding digermane $\text{Pr}^i_3\text{GeGePh}_3$ (**3**) in high (87%) yield. However, this reaction proceeded significantly more slowly than involving the phenyl derivative **1a**, requiring reaction times of between 32 and 36 h for complete consumption of the starting materials. The reactivity of $\text{Et}_3\text{GeCH}_2\text{CN}$ with various substrates has been investigated



Scheme 1.

which demonstrated the lability of the Ge–CH₂CN bond in this compound [61]. However, the reactivity of other α -germylated nitriles has not been described and the reported lability of the Ge–C bonds in these compounds appears to be highly dependent on the substituents attached to germanium, where the presence of sterically demanding or electron withdrawing groups can significantly retard reactions involving cleavage of the Ge–C bond.

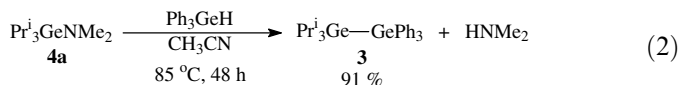
Since the α -germylated nitrile reagents are more difficult to prepare than the corresponding amides and do not provide the Ge–Ge bonded species more rapidly in a general sense, there is little advantage to employing the –CH₂CN versus the –NMe₂ ligand in reagents for the construction of Ge–Ge bonds. Therefore, the germanium amide reagents Pr₃GeNMe₂ (**4a**) and Bu₃GeNMe₂ (**4b**) were also prepared by the metathesis reaction of the corresponding chlorides and LiNMe₂. The *iso*-propyl derivative **4a** could be synthesized in benzene or THF solvent at room temperature but synthesis of **4b** required refluxing the two reagents in THF for 24 h due to the steric crowding about the germanium atom. The ¹H NMR spectra of these species contain characteristic resonances for the protons of the amide groups at δ 2.67 (**4a**) and 2.71 (**4b**) ppm in C₆D₆ solvent and elemental analyses for both compounds were also successfully obtained.

The digermene Pr₃GeGePh₃ (**3**) could be obtained in slightly higher yield (91%) versus the reaction of **1b** and Ph₃GeH when using the amide reagent **4a** as the starting material (Eq. (2)). Compound **3** was characterized by NMR (¹H and ¹³C) spectroscopy and elemental analysis, where resonances for the methyl and methine protons of the *iso*-propyl groups appear as a doublet at δ 1.18 ppm and a septet at δ 1.67 ppm ($J = 7.5$ Hz) in C₆D₆ solvent, respectively. The X-ray crystal structure of **3** was deter-

Table 1
Selected bond distances (Å) and angles (°) for Pr₃GeGePh₃ (**3**)

Ge(1)–Ge(2)	2.4637(7)	C(1)–Ge(1)–Ge(2)	105.04(6)
Ge(1)–C(1)	1.990(2)	C(4)–Ge(1)–Ge(2)	113.64(6)
Ge(1)–C(4)	1.980(2)	C(7)–Ge(1)–Ge(2)	110.11(6)
Ge(1)–C(7)	1.986(2)	C(10)–Ge(2)–C(16)	107.01(8)
Ge(2)–C(10)	1.964(2)	C(10)–Ge(2)–C(22)	107.34(8)
Ge(2)–C(16)	1.960(2)	C(16)–Ge(2)–C(22)	107.90(8)
Ge(2)–C(22)	1.961(2)	C(10)–Ge(2)–Ge(1)	107.95(6)
C(1)–Ge(1)–C(4)	105.87(9)	C(16)–Ge(2)–Ge(1)	115.14(6)
C(1)–Ge(1)–C(7)	110.27(9)	C(22)–Ge(2)–Ge(1)	111.16(6)
C(4)–Ge(1)–C(7)	111.60(9)		

mined and an ORTEP diagram is shown in Fig. 1 while selected bond distances and angles are collected in Table 1. The three sterically encumbering *iso*-propyl groups in **3** result in a Ge–Ge distance of 2.4637(7) Å, which is longer than the corresponding bond lengths in Me₃GeGePh₃ (**5**, 2.418(1) Å) [66], Et₃GeGePh₃ (**6**, 2.4253(7) Å) [60], Bu₃GeGePh₃ (**7**, 2.4208(8) Å) [60], and Ph₃GeGePh₃ (**2**, 2.446(1) Å) [32]. The average Ge–C_{aliphatic} distance in **3** is 1.985(2) Å which is significantly longer than those of **5–7** which range from 1.943 to 1.959 Å. The average Ge–C_{ipso} distance (1.962(2) Å) in **3** is also elongated versus those in **2** and **5–7** (1.954(2)–1.957(2) Å). The average C–Ge–C angles among **3** and **5–7** for the aliphatic substituents approach normal values for a tetrahedral geometry at germanium ranging from 108.7(1) to 109.75(9)°, while those for the phenyl substituents in **2**, **3**, and **5–7** are generally more obtuse ranging from 108.1(3)° to 111.51(6)°.



The synthesis of Bu₃GeGePh₃ starting from **4b** and Ph₃GeH was attempted but no evidence for the formation of this product was found. Vacuum distillation of the crude product mixture obtained from the reaction of **4b** with Ph₃GeH in CH₃CN at 120 °C afforded a small amount (0.025 g) of unreacted **4b** and continued distillation at 180 °C resulted in the isolation of a yellow solid material which, upon recrystallization from cold hexane, furnished Bu₃Ge[NHC(CH₃)CHCN] (**8**) as a minor product with a maximum yield of 6% (Eq. (3)) over three separate trials. Unreacted Ph₃GeH and Bu₃GeCH₂CN were also contained in this second fraction as shown by ¹H NMR spectroscopy.

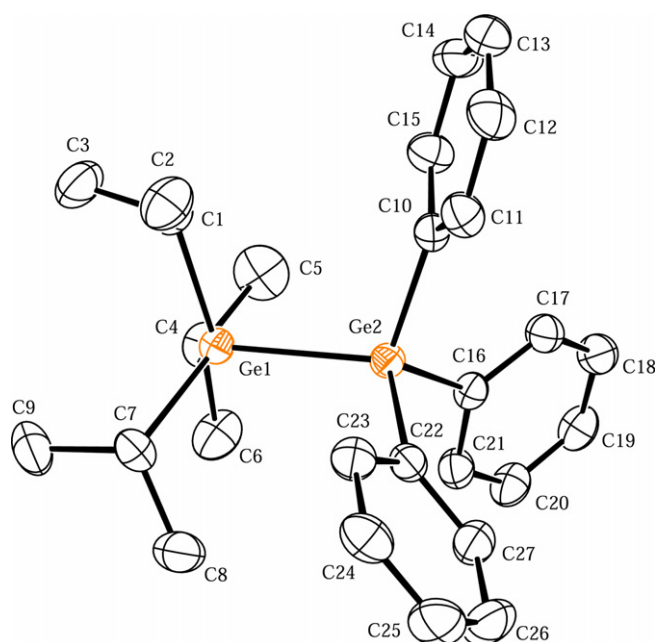
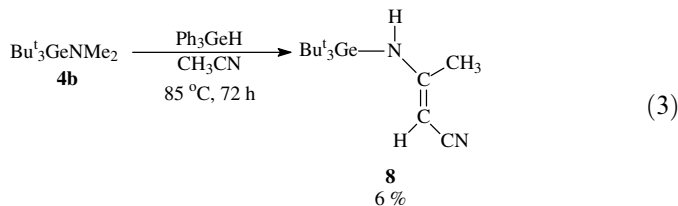


Fig. 1. ORTEP diagram of Pr₃GeGePh₃ (**3**). Thermal ellipsoids are drawn at 50% probability.

The pathway for this reaction was probed using ¹³C NMR spectroscopy in CD₃CN solvent which indicated that the presence of Ph₃GeH was necessary for the

generation of both $\text{Bu}_3\text{GeCH}_2\text{CN}$ and compound **8**. The appearance of the ^{13}C NMR spectrum after heating **4b** alone in CD_3CN for 6 days at 85°C was unchanged with the resonance for the carbon atoms of the $-\text{NMe}_2$ groups at δ 42.2 ppm remaining present. However, heating the sample for 24 h after the addition of 1 equiv. of Ph_3GeH resulted a significant decrease in intensity of this feature as well as the corresponding resonance for the *tert*-butyl groups of **4b**. After continued heating for 72 h, the appearance of peaks at δ 135.8, 130.3, and 129.5 ppm indicated the presence of the deuterated analog of **8**, and features for Ph_3GeH and $\text{Bu}_3\text{GeCD}_2\text{CN}$ were also present. The appearance of the ^{13}C NMR spectrum remained unchanged upon heating the sample for a further 72 h. These results are consistent with those obtained from the preparative scale reaction where a small amount of unreacted **4b** was recovered in the low boiling fraction (*vide supra*).

It is likely that compound **8** is generated by a variation of the Thorpe reaction used for the dimerization of nitriles which requires the presence of a base in either catalytic or stoichiometric amounts [67]. Although Ph_3GeH cannot be considered a base, it is required for the generation of both the α -germylated nitrile **1c** and compound **8** from Bu_3GeCl but is not consumed to any significant degree in the process and so appears to function as a catalyst. Although the exact role of Ph_3GeH is not known, a proposed pathway for the formation of **8** is shown in Scheme 2.

The ^1H NMR spectrum of **8** in C_6D_6 contains a single resonance at δ 1.08 ppm for the *tert*-butyl groups as well as sharp signals at δ 1.94 and 4.33 ppm corresponding to the protons of the methyl group and the single olefinic proton (respectively), while a broad singlet at δ 3.18 ppm arises from the proton bound to nitrogen. The presence of only one feature for each type of proton in the 3-amidocrotononitrile ligand in **8** indicates the substituents about the $\text{C}=\text{C}$ double bond are present in only one conformation.

In order to ascertain the exact conformation of the ligand, the X-ray crystal structure of **8** was determined. An ORTEP diagram of **8** is shown in Fig. 2 while bond distances and angles are collected in Table 2. The 3-amidocrotononitrile ligand exclusively adopts an (*E*)-configuration

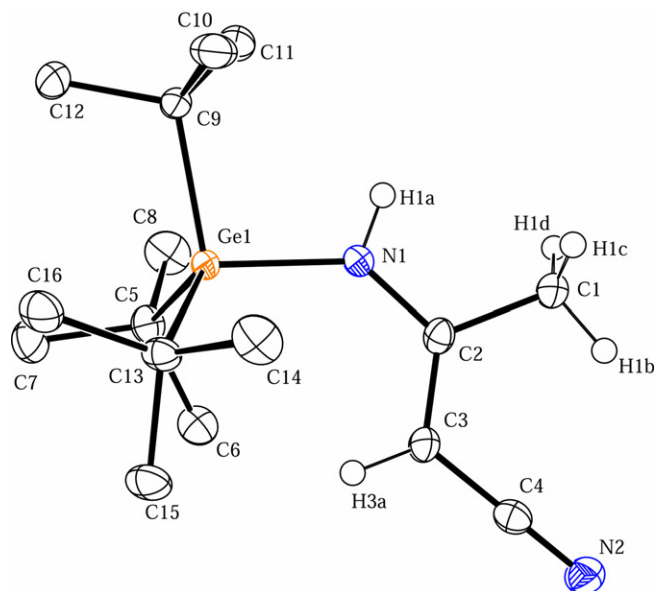


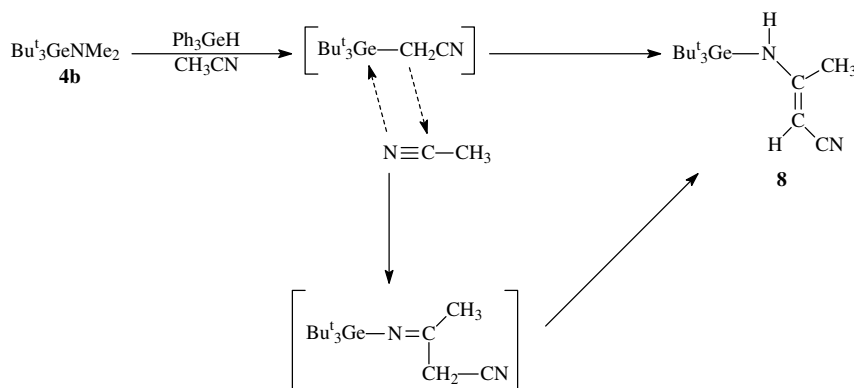
Fig. 2. ORTEP diagram of $\text{Bu}_3\text{GeNHC}(\text{CH}_3)\text{CHCN}$ (**8**). Thermal ellipsoids are drawn at 50% probability.

Table 2

Selected bond distances (Å) and angles ($^\circ$) for $\text{Bu}_3\text{GeNHC}(\text{CH}_3)\text{CHCN}$ (**8**)

Ge(1)–N(1)	1.895(2)	C(5)–Ge(1)–C(9)	112.76(9)
Ge(1)–C(5)	2.006(2)	C(5)–Ge(1)–C(13)	113.61(8)
Ge(1)–C(9)	2.015(2)	C(9)–Ge(1)–C(13)	112.47(9)
Ge(1)–C(13)	2.018(2)	Ge(1)–N(1)–C(2)	135.4(1)
N(1)–C(2)	1.360(3)	N(1)–C(2)–C(1)	115.6(2)
C(1)–C(2)	1.509(3)	N(1)–C(2)–C(3)	125.0(2)
C(2)–C(3)	1.361(3)	C(1)–C(2)–C(3)	119.5(2)
C(3)–C(4)	1.414(3)	C(2)–C(3)–C(4)	121.4(2)
C(4)–N(2)	1.152(3)	C(3)–C(4)–N(2)	179.6(3)
N(1)–Ge(1)–C(5)	108.76(8)		
N(1)–Ge(1)–C(9)	99.25(7)		
N(1)–Ge(1)–C(13)	108.90(8)		

about the $\text{C}=\text{C}$ double bond which measures 1.361(3) Å. Crystallographically characterized Ge compounds bearing a single Ge–N bond are rare, and this distance in **8** is 1.895(2) Å which is longer than the Ge–N distances of



Scheme 2.

1.854(3), 1.818(2), and 1.824(9) Å in the primary germyl-amines $\text{Mes}_3\text{GeNH}_2$ [68], $(\text{RGe})_2(\text{NH}_2)_4(\text{NH})$ ($\text{R} = \text{Pr}^i_2\text{C}_6\text{H}_3\text{NSiMe}_3$) [69], and $[(2,6\text{-Pr}^i_2\text{C}_6\text{H}_3)\text{NSiMe}_3\text{Ge}(\text{NH}_2)\text{NH}]_3$ [70] (respectively). However, the Ge–N bond length in **8** is similar to those in the germanium(IV) compounds $[(\text{Me}_3\text{Si})_2\text{N}]_3\text{GeBr}$ (1.848(3) Å) and $[(\text{Me}_3\text{Si})_2\text{N}]_3\text{GeBu}$ (1.890(2) Å) [71], and also compares with the Ge–N distances in the germanium(II) amides $\text{Ge}[\text{N}(\text{SiMe}_3)_2]_2$ [72] and $\text{Ge}[\text{NC}_6\text{H}_6(\text{CH}_3)_4\text{-}2,2,6,6]_2$ [73] which are 1.875(5) and 1.88(5) Å (respectively). The environment about the germanium atom in **8** is distorted tetrahedral with the largest perturbation occurring in the C–Ge–C angles which average $112.95(8)^\circ$. This distortion occurs due to the presence of the three bulky *tert*-butyl groups which also results in the long average Ge–C bond length of 2.013(2) Å. This distance is elongated by 0.07 Å relative to typical Ge–C single bonds (1.94 Å) [74], but is significantly shorter than the average Ge–C bond length in $\text{Bu}_3^i\text{GeGeBu}_3$ which is 2.076(7) Å [53].

3. Conclusions

We have demonstrated that the reactions of germanium amides R_3GeNMe_2 ($\text{R} = \text{Ph}, \text{Pr}^i$) with Ph_3GeH in CH_3CN solution proceed via conversion of the amide to an α -germylated nitrile $\text{R}_3\text{GeCH}_2\text{CN}$ which is the active species in the Ge–Ge bond forming reaction. The intermediate $\text{R}_3\text{GeCH}_2\text{CN}$ reagents, which can also be directly synthesized from the chlorides R_3GeCl and LiCH_2CN , reacts with Ph_3GeH to furnish the digermans and CH_3CN . The lability of the Ge–C bond in the α -germylated nitriles appears to depend on the steric and/or electronic attributes of the organic substituents attached to germanium, with reactions involving the phenyl-substituted derivative proceeding more rapidly than those of the *iso*-propyl-substituted species.

Treatment of either $\text{Bu}_3^i\text{GeCH}_2\text{CN}$ or $\text{Bu}_3^i\text{GeNMe}_2$ with Ph_3GeH did not result in isolation of the expected digermane $\text{Bu}_3^i\text{GeGePh}_3$ but rather generated the 3-amidocrotonitrile-containing germane $\text{Bu}_3^i\text{Ge}[\text{NHC}(\text{CH}_3)\text{CHCN}]$ as a minor product. The nitrogen-containing substituent in this compound results from reaction of $\text{Bu}_3^i\text{GeCH}_2\text{CN}$ with a further equivalent of CH_3CN and the 3-amidocrotonitrile ligand is present exclusively in the (*E*)-configuration.

4. Experimental

4.1. General remarks

All manipulations were carried out using standard Schlenk, syringe, and glovebox techniques [75]. The reagents GeCl_4 , Pr^i_3GeCl , Ph_3GeCl , and Ph_3GeH were purchased from Gelest, Inc. and used as received, and CuCN and Bu^iLi (1.7 M in pentane) were purchased from Aldrich while LiNPr^i_2 was prepared *in situ* from HNPr^i_2 and Bu^nLi . The reagent LiCH_2CN was prepared according to a literature procedure [63], and our modification of the reported

synthesis [53] of Bu_3^iGeCl is described below. Solvents were purified using a Glass Contour solvent purification system. NMR spectral data were recording using a Varian Gemini 2000 spectrometer operating at 300 MHz (^1H) or 75.5 MHz (^{13}C) and were referenced to resonances for the solvent. Elemental analyses were conducted by Desert Analytics (Tucson, Az) or Midwest Microlabs (Indianapolis, IN).

4.2. Synthesis of Bu_3^iGeCl

To a suspension of CuCN (11.55 g, 0.129 mol) in THF (75.5 mL) cooled to -25°C in a *meta*-dichlorobenzene/liquid N_2 bath was added a solution of 1.7 M Bu^iLi in pentane (75.8 mL, 0.129 mol) dropwise over 1 h. The resulting suspension was cooled to -40°C using a CH_3CN /liquid N_2 bath and neat GeCl_4 (9.25 g, 0.043 mmol) was slowly added. The THF was removed *in vacuo* and exchanged for 65 mL of a 1:1 mixture of hexane and benzene. The insoluble salts were removed by filtration and the solvent was distilled off under N_2 . The resulting oil was vacuum distilled at 0.010 torr and 150°C to yield Bu_3^iGeCl (4.311 g, 36%) as a colorless oil. ^1H NMR (C_6D_6 , 25°C) δ 1.11 (s, 27H, $-\text{C}(\text{CH}_3)_3$) ppm. ^{13}C NMR (C_6D_6 , 25°C) δ 29.8 ($-\text{C}(\text{CH}_3)_3$), 31.3 ($-\text{C}(\text{CH}_3)_3$) ppm.

4.3. Synthesis of $\text{Ph}_3\text{GeCH}_2\text{CN}$ (**1a**)

A solution of LiCH_2CN was prepared from CH_3CN (0.10 mL, 1.91 mmol) and LiNPr^i_2 (0.212 g, 1.98 mmol) and stirred at -78°C for 30 min. To this was added a solution of Ph_3GeCl (0.666 g, 1.96 mmol) in THF (20 mL) at -78°C . The reaction mixture was warmed to room temperature and stirred for 12 h. The volatiles were removed *in vacuo* to yield a white semisolid which was suspended in hexane and filtered through Celite. Removal of the solvent furnished $\text{Ph}_3\text{GeCH}_2\text{CN}$ (0.472 g, 70%) as a white solid. ^1H NMR (C_6D_6 , 25°C) δ 7.43 (d, 6H, *o*- C_6H_5), 7.08–7.00 (m, 9H, aromatics), 1.98 (s, 2H, $-\text{CH}_2\text{CN}$) ppm. ^{13}C NMR (C_6D_6 , 25°C) δ 132.5, 128.4, 126.9, 125.1, 124.2, 20.2 ppm.

4.4. Synthesis of $\text{Pr}^i_3\text{GeCH}_2\text{CN}$ (**1b**)

The same procedure for the preparation of **1a** was used for **1b** starting with Pr^i_3GeCl (0.422 g, 1.78 mmol), CH_3CN (95 μL , 1.82 mmol) and LiNPr^i_2 (0.195 g, 1.82 mmol) and **1b** was isolated as a colorless oil. Yield = 0.358 g, 83%. ^1H NMR (C_6D_6 , 25°C) δ 1.62 (sept, $J = 7.2$ Hz, 3H, $(\text{CH}_3)_2\text{CH}$), 1.43 (s, 2H, $-\text{CH}_2\text{CN}$), 1.18 (d, $J = 7.2$ Hz, 18H, $(\text{CH}_3)_2\text{CH}$) ppm. ^{13}C NMR (C_6D_6 , 25°C) δ 118.4 ($-\text{CH}_2\text{CN}$), 24.6 ($-\text{CH}_2\text{CN}$), 19.3 ($(\text{CH}_3)_2\text{CH}$), 14.8 ($(\text{CH}_3)_2\text{CH}$) ppm.

4.5. Synthesis of $\text{Bu}_3^i\text{GeCH}_2\text{CN}$ (**1c**)

The same procedure for the preparation of **1a** was used for **1c** starting with Bu_3^iGeCl (0.225 g, 0.805 mmol),

CH₃CN (44 μ L, 0.84 mmol) and LiNPr₂ⁱ (0.090 g, 0.84 mmol) and **1c** was isolated as a colorless oil. Yield = 0.147 g, 64%. ¹H NMR (C₆D₆, 25 °C) δ 1.59 (s, 2H, –CH₂CN), 1.06 (s, 27H, –C(CH₃)₃) ppm. ¹³C NMR (C₆D₆, 25 °C) δ 123.2 (–CH₂CN), 31.4 (–C(CH₃)₃), 30.2 (–C(CH₃)₃), 28.3 (–CH₂CN) ppm.

4.6. Preparation of Ph₃GeGePh₃(2) using **1a**

The same procedure used for the synthesis of **3** (Section 4.10, *vide infra*) from **4a** was employed starting with **1a** (0.315 g, 0.916 mmol) and Ph₃GeH (0.282 g, 0.925 mmol) yielding Ph₃GeGePh₃ (**2**) (0.488 g, 88%). Anal. Calc. for C₃₆H₃₀Ge₂: C, 71.14; H, 4.97. Found: C, 71.02; 5.04%.

4.7. Preparation of Ph₃GeGePrⁱ₃ (**3**) using **1b**

The same procedure used to prepare **3** from **4a** (Section 4.10, *vide infra*) was employed starting with **1b** (0.255 g, 1.05 mmol) and Ph₃GeH (0.332 g, 1.09 mmol) yielding **3** (0.461 g, 87%).

4.8. Preparation of Prⁱ₃GeNMe₂ (**4a**)

To a solution of Prⁱ₃GeCl (1.00 g, 4.21 mmol) in benzene (15 mL) was added a suspension of LiNMe₂ (0.225 g, 4.42 mmol) in benzene (20 mL). The resulting suspension was stirred for 24 h and then filtered through Celite. The volatiles were removed from the filtrate *in vacuo* to yield **4a** (0.778 g, 75%) as a colorless oil. ¹H NMR (C₆D₆, 25 °C) δ 2.67 (s, 6H, –N(CH₃)₂), 1.42 (sept, *J* = 7.2 Hz, 3H, CH₃CHCH₃), 1.10 (d, *J* = 7.2 Hz, 18H, CH₃CHCH₃) ppm. ¹³C NMR (C₆D₆, 25 °C) δ 42.2 (–N(CH₃)₂), 18.8 (CH₃CHCH₃), 15.7 (CH₃CHCH₃) ppm. Anal. Calc. for C₁₁H₂₇GeN: C, 53.72; H, 11.07. Found: C, 53.81; H, 11.11%.

4.9. Synthesis of Buⁱ₃GeNMe₂ (**4b**)

To a solution of Buⁱ₃GeCl (0.500 g, 1.79 mmol) in THF (20 mL) was added a solution of LiNMe₂ (0.091 g, 1.79 mmol) in THF (10 mL). The reaction mixture was refluxed for 18 h and the solvent was removed *in vacuo*. The resulting solid was dissolved in benzene, filtered through Celite, and the volatiles were removed *in vacuo* to yield a pale yellow semisolid. The crude product was distilled in a Kugelrohr oven (125 °C, 0.07 torr) to yield **4b** (0.315 g, 61%) as a colorless oil. ¹H NMR (C₆D₆, 25 °C) δ 2.71 (s, 6H, –N(CH₃)₂), 1.19 (s, 27H, –C(CH₃)₃) ppm. ¹H NMR (CD₃CN, 25 °C) δ 2.63 (s, 6H, –N(CH₃)₂), 1.27 (s, 27H, –C(CH₃)₃) ppm. ¹³C NMR (C₆D₆, 25 °C) δ 41.9 (–N(CH₃)₂), 32.8 (–C(CH₃)₃), 29.9 (–C(CH₃)₃) ppm. ¹³C NMR (CD₃CN, 25 °C) δ 42.2 (–N(CH₃)₂), 31.6 (–C(CH₃)₃), 30.2 (–C(CH₃)₃) ppm. Anal. Calc. for C₁₄H₃₃GeN: C, 58.38; H, 11.55. Found: C, 58.03; H, 11.67%.

4.10. Preparation of Prⁱ₃GeGePh₃ (**3**) using **4a**

To a solution of **4a** (0.778 g, 3.16 mmol) in acetonitrile (20 mL) in a Schlenk tube was added a solution of Ph₃GeH (1.239 g, 4.062 mmol) in acetonitrile (10 mL). The tube was sealed and the reaction mixture was heated at 85 °C for 48 h. The volatiles were removed *in vacuo* and the crude product was distilled in a Kugelrohr oven (180 °C, 0.05 torr) to remove excess Ph₃GeH which furnished **3** (1.451 g, 91%) as a colorless solid. ¹H NMR (C₆D₆, 25 °C) δ 7.72–7.68 (m, 6H, *meta*-H), 7.20–7.15 (m, 9H, *para*- and *ortho*-H), 1.67 (sept, *J* = 7.5 Hz, 3H, CH₃CHCH₃), 1.18 (d, *J* = 7.5 Hz, 18H, CH₃CHCH₃) ppm. ¹³C NMR (C₆D₆, 25 °C) δ 139.8 (*ipso*-C), 135.9 (*ortho*-C), 128.6 (*meta*-C), 128.5 (*para*-C), 21.3 (CH₃CHCH₃), 16.8 (CH₃CHCH₃) ppm. UV–Vis: λ_{\max} 234 nm (br, ϵ 3.82 \times 10⁴ cm^{–1} M^{–1}). Anal. Calc. for C₂₇H₃₆Ge₂: C, 64.12; H, 7.17. Found: C, 63.88; H, 6.97%.

4.11. Preparation of Buⁱ₃Ge[NHC(CH₃)CHCN] (**8**)

To a solution of **4b** (0.281 g, 0.976 mmol) in CH₃CN (5 mL) was added a solution of Ph₃GeH (0.299 g, 0.981 mmol) in CH₃CN (10 mL). The reaction mixture was sealed in a Schlenk tube and was heated at 85 °C for 72 h. The solvent was removed *in vacuo* to yield a yellow oil. The crude material was distilled in a Kugelrohr oven (120 °C, 0.050 torr) resulting in the collection of a clear oil which was isolated (0.147 g) and identified to be pure Buⁱ₃GeNMe₂. A new receiving flask was attached to the apparatus and distillation was continued (180 °C, 0.05 torr) resulting in the isolation of a yellow oil (0.338 g) which consisted of a mixture of **8**, **4b**, and Ph₃GeH as shown by ¹H NMR spectroscopy. Recrystallization of the product from hexane (~3 mL) at –35 °C afforded **8** as colorless crystals (0.020 g, 6.3%). ¹H NMR (C₆D₆, 25 °C) δ 4.33 (s, 1H, C=CHCN), 3.18 (br s, 1H, Ge–NH), 1.94 (s, 3H, H₃C–C=C), 1.08 (s, 28H, –C(CH₃)₃) ppm. ¹H NMR (CD₃CN, 25 °C) δ 4.09 (s, 1H, C=CHCN), 3.84 (br s, 1H, Ge–NH), 2.14 (s, 3H, H₃C–C=C), 1.25 (s, 28H, –C(CH₃)₃) ppm. ¹³C NMR (CD₃CN, 25 °C) δ 135.8 (–CN), 130.2 (N–C=C), 129.4 (N–C=C), 66.0 (C=C–CH₃), 31.5 (–C(CH₃)₃), 30.7 (–C(CH₃)₃) ppm. Anal. Calc. for C₁₆H₃₂GeN₂: C, 59.13; H, 9.92. Found: C, 58.92; H, 9.97%.

4.12. NMR tube reaction of Buⁱ₃GeNMe₂ with Ph₃GeH

A solution of **4b** (0.025 g, 0.087 mmol) in CD₃CN (0.5 mL) was prepared in a Kontes screw-cap NMR tube. The sample was heated at 85 °C for 6 days during which time the ¹³C NMR spectrum was recorded at regular intervals. After this time, Ph₃GeH (0.027, 0.088 mmol) was added to the tube and the sample was heated at 85 °C for 24 h. The ¹³C NMR spectrum was recorded and the sample was heated at 85 °C for a further 72 h.

4.13. X-ray crystal structure of compounds **3** and **8**

Diffraction intensity data were collected with a Siemens P4/CCD diffractometer. Crystallographic data and details of X-ray studies are shown in Table 3. Absorption corrections were applied for all data by SADABS. The structures were solved using direct methods, completed by difference Fourier syntheses, and refined by full matrix least squares procedures on F^2 . All non-hydrogen atoms were refined with anisotropic displacement coefficients and hydrogen atoms were treated as idealized contributions. All software and sources of scattering factors are contained in the SHELXTL (5.10) program package (G. Sheldrick, Bruker XRD, Madison, WI). ORTEP diagrams were drawn using the ORTEP3 program (L.J. Farrugia, Glasgow).

Table 3
Crystal data and structure refinement details for **3** and **8**

	$C_{27}H_{36}Ge_2$ (3)	$C_{16}H_{32}GeN_2$ (8)
Empirical formula	$C_{27}H_{36}Ge_2$ (3)	$C_{16}H_{32}GeN_2$ (8)
Formula weight (g/mol)	505.74	325.03
Temperature (K)	208(2)	100(2)
Wavelength (Å)	0.71069	0.71073
Crystal system	Triclinic	Monoclinic
Space group	$P\bar{1}$	$P2_1/c$
<i>a</i> (Å)	8.786(2)	14.2022(8)
<i>b</i> (Å)	9.361(3)	8.4666(5)
<i>c</i> (Å)	15.544(4)	14.9069(8)
α (°)	90.138(5)	90
β (°)	90.176(5)	93.932(1)
γ (°)	102.212(5)	90
Volume (Å ³)	1249.5(6)	1788.2(2)
<i>Z</i>	2	4
Calculated density (g/cm ³)	1.344	1.207
Absorption coefficient (mm ⁻¹)	2.416	1.705
<i>F</i> (000)	524	696
Crystal size (mm)	0.14 × 0.10 × 0.07	0.35 × 0.30 × 0.28
Crystal color and shape	Colorless block	Colorless block
θ Range for data collection (°)	2.23–28.27	1.44–28.21
Index ranges	–11 ≤ <i>h</i> ≤ 11, –12 ≤ <i>k</i> ≤ 12, –20 ≤ <i>l</i> ≤ 20	–14 ≤ <i>h</i> ≤ 17, –10 ≤ <i>k</i> ≤ 10, –19 ≤ <i>l</i> ≤ 19
Reflections collected	15365	12764
Independent reflections	5760 ($R_{int} = 0.0316$)	3935 ($R_{int} = 0.0279$)
Completeness to θ	25.00 (99.8%)	25.00 (97.6%)
Absorption correction	Semi-empirical from equivalents	Multi-scan
Maximum and minimum transmission	0.8491 and 0.7285	0.6467 and 0.5867
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	5760/0/268	3935/0/172
Goodness of fit on F^2	1.067	1.020
Final <i>R</i> indices ($I > 2\sigma(I)$)		
<i>R</i> ₁	0.0335	0.0296
<i>wR</i> ₂	0.0892	0.0689
Final <i>R</i> indices (all data)		
<i>R</i> ₁	0.0376	0.0388
<i>wR</i> ₂	0.0923	0.0733
Largest difference in peak and hole (e Å ⁻³)	1.126 and –0.817	0.486 and –0.436

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Appendix A. Supplementary material

CCDC 670761 and 670763 contain the supplementary crystallographic data for **8** and **5**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.jorganchem.2008.01.045](https://doi.org/10.1016/j.jorganchem.2008.01.045).

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