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Reactivity of α-germyl nitriles with acetonitrile: Synthesis, structures, and generation of $Ph_3Ge[NHC(CH_3)CHCN]$ and 2,6-dimethyl-4-(triphenylgermylamino)pyrimidine from Ph_3GeCH_2CN

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ABSTRACT

The formation of 3-aminocrotononitrile and 4-amino-2,6-dimethylaminopyrimidine has been observed during the course of the hydrogermolysis reaction between a germanium amide and a germanium hydride, either as the free amines or bound to germanium as ligands consisting of their conjugate bases. These species arise from the dimerization or trimerization of acetonitrile, and have only been detected when germanium amides having substantial steric bulk at the germanium center are employed in the reaction. The isolation of germanium-bound 3-aminocrotononitrile compounds suggests that α-germyl nitrile species R_3GeCH_2CN that result from the reaction of the germanium amides R_3GeNMe_2 with CH_3CN solvent also can further react with CH_3CN to generate the 3-aminocrotononitrile and 4-amido-2,6-dimethylaminopyrimidine species. The two germanes $Ph_3Ge[NHC(CH_3)=CHCN]$ and 2,6-dimethyl-4-(triphenylgermylamino)pyrimidine have been prepared and structurally characterized, and the conversion of Ph_3GeCH_2CN to $Ph_3Ge[NHC(CH_3)=CHCN]$ and 2,6-dimethylamino-4-(triphenylgermylamino)pyrimidine as well as the conversion of $Ph_3Ge[NHC(CH_3)=CHCN]$ to 2,6-dimethyl-4-(triphenylgermylamino)pyrimidine in acetonitrile solvent has been observed using ^1H NMR spectroscopy.

1. Introduction

The hydrogermolysis reaction between a germanium amide and a germanium hydride has proven to be a useful tool for the formation of germanium–germanium single bonds, and has been shown to proceed via the *in situ* conversion of the germanium amide to an α-germyl nitrile that is the active species in the Ge–Ge bond forming process [1–11]. Using this method, both linear and branched oligogermane systems having up to seven germanium atoms in the Ge–Ge backbone have been prepared. However, some steric limitations to this process have been realized.

We have observed the formation of both 3-aminocrotononitrile (**1**) and 4-amino-2,6-dimethylaminopyrimidine (**2**) during the hydrogermolysis reaction when bulky germanium amides have been employed as reactants. Specifically, the attempted synthesis of $(Ph_3Ge)_4Ge$ from $(Ph_3Ge)_3GeNMe_2$ and Ph_3GeH yielded a mixture of products that included **1** and **2** [8,9], and the attempted synthesis of $Ph_3GeGeBu^t_3$ from Ph_3GeH and $Bu^t_3GeNMe_2$ generated the 3-amidocrotononitrile-substituted germane $Bu^t_3Ge[NHC(CH_3)=CHCN]$ (**3**), where the free amine **1** is present as a nitrogen-bound ligand at germanium [1]. The free amines **1** and **2**, as well as the germanium–bound ligand in **3**, result from the dimerization or trimerization of acetonitrile that occurs via the Thorpe reaction which is a general method for the base-catalyzed self-condensation of aliphatic nitriles [12,13]. We have prepared the germanes $Ph_3Ge[NHC(CH_3)=CHCN]$ (**4**) and 2,6-dimethyl-4-(triphenylgermylamino)pyrimidine (**5**) from the corresponding amines **1** and **2** and Ph_3GeCl, have determined their X-ray crystal structures, and have investigated the *in situ* conversion of Ph_3GeCH_2CN to **4** and the subsequent conversion of **4** to **5**.

2. Results and discussion

Compound **4** was prepared from a commercial sample of 3-aminocrotononitrile which contained both the (*E*)- and (*Z*)-isomers. The ^1H NMR spectrum of the starting material indicated that the two isomers were present in an approximate 2:1 (*Z*):(*E*) ratio. Treatment 3-aminocrotononitrile with one equiv. of Bu^nLi in THF yielded the monolithium salt $LiNHC(CH_3)CHCN$ that was

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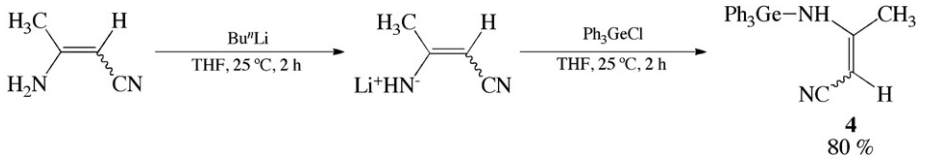


Scheme 1. Synthesis of $Ph_3Ge[NHC(CH_3)=CHCN$ (**4**).

subsequently added to Ph_3GeCl in THF to yield the germanium compound **4** in 80% yield (Scheme 1). After isolation and purification of the product mixture the ^1H NMR of **4** indicated that both isomers of the 3-amidocrotononitrile ligand were present in an approximate 1:1 isomeric ratio. Two sets of resonances for the hydrogen atoms of the 3-amidocrotononitrile ligand were visible in the ^1H NMR spectrum of **4** at δ 4.06, 3.49, 1.78 ppm for the (*E*)-isomer and δ 3.76, 3.62, 1.42 ppm for the (*Z*)-isomer, where these features correspond to the olefinic, amide, and methyl group protons (respectively) in each case. The resonance for the olefinic proton in the (*Z*)-isomer is expected to appear at higher field since it is disposed *trans*- to the amino group due to the stronger *trans*-interaction [14].

After heating the isolated material at 85 °C in CH_3CN for 7 days the material had completely isomerized to the (*E*)-isomer and it has been noted that this species is more stable than the (*Z*)-isomer [15]. The ^1H NMR in benzene-d_6 of the isolated material exhibited the aforementioned three singlets at δ 4.06, 3.49, 1.78 ppm. The resonance for the amide proton appears upfield from that of the free amine (δ 4.69 (*E*) or 4.40 (*Z*) ppm) due to the attachment of the nitrogen atom to germanium, but this feature is shifted downfield relative to that for **3** due to the presence of electron-withdrawing phenyl substituents at germanium in **4** versus the *tert*-butyl groups in **3**.

Recrystallization of this material from hot benzene yielded X-ray quality crystals, and an ORTEP diagram of **4** is shown in Fig. 1 and selected bond distances and angles are collected in Table 1. The environment at germanium is distorted from idealized tetrahedral, and the average C_{ipso}–Ge–C_{ipso} bond angle is 111.14(7)° and the average C_{ipso}–Ge–N bond angle is 107.7(7)°. The corresponding angles in the *tert*-butyl-substituted compound **3** are 112.95(8) and 105.64(7)° indicating that the structure of **3** is slightly more distorted from the ideal geometry than that of **4**, as expected. The nitrogen atoms of the 3-amidocrotononitrile ligand in both **3** and **4** are not pyramidal but rather adopt a distorted trigonal planar geometry where the Ge–N–C bond angles are 135.4(1) and 129.75(2)° for **3** and **4** (respectively). In both of these molecules, the lone pair of electrons at nitrogen is conjugated with the C–C double bond and the C–N triple bond in the ligand resulting in a planar geometry at nitrogen. The distortion of the Ge–N–C bond angle from the idealized value of 120° results from the steric congestion at the neighboring germanium atom, and the greater distortion in **3** versus **4** is attributable to the higher steric demands of the *tert*-butyl groups present in **3**. In addition, all of the carbon and nitrogen atoms of the 3-amidocrotononitrile ligand are coplanar in both structures.

The 3-amidocrotononitrile ligand is present exclusively in the (*E*)-configuration in the crystal structure of **4**, which was also found for the related *tert*-butyl substituted analogue (**3**) [1] as well as for the free amine **1** that was isolated from the reaction of $(Ph_3Ge)_3$-$GeNMe_2$ with Ph_3GeH [8,9]. The presence of the less sterically demanding phenyl groups at the germanium center in **4** versus the *tert*-butyl substituents in **3** has the most pronounced effect on the structure of these molecules in the vicinity of the Ge–N bond. The Ge–N distance in **4** is 1.866(1) Å and is shorter than that in **3** (1.895(2) Å) by 0.029 Å while the remaining bond distances and angles in the 3-amidocrotononitrile ligand of **4** and those in **3** are nearly identical. Similarly, the Ge–N–Cα bond angles in **4** and **3** also differ significantly, measuring 129.8(1) and 135.4(1)° (respectively), but the remaining bond angles within the 3-amidocrotononitrile ligands of these two species are nearly identical. In both compounds, the bond distances and angles between the Cα–Cβ atoms clearly indicate the presence of a C=C double bond, and the C–CN bond angles in both compounds are nearly linear, as expected.

The structure of free 3-aminocrotononitrile (**1**) has also been reported [9], and closely resembles the ligands of **3** and **4** with the exception of the environment about the N–Cα bond. The N–Cα bond in the free amine measures 1.346(1) Å and the N–Cα–Cβ bond

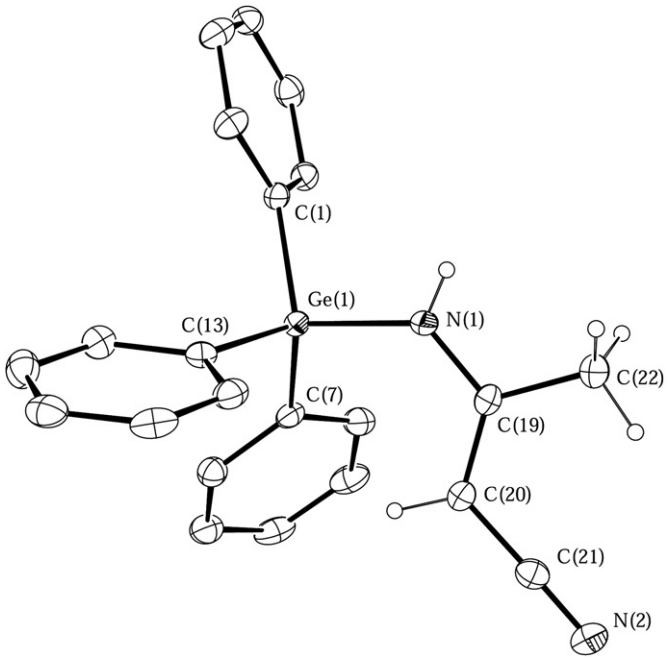
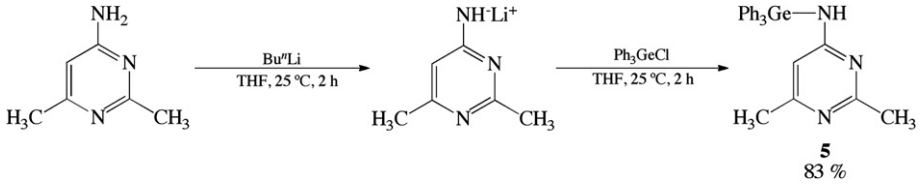


Fig. 1. ORTEP diagram of $Ph_3Ge[NHC(CH_3)CHCN]$ (**4**). Thermal ellipsoids are drawn at 50% probability.

Table 1
Bond distances (Å) and angles (°) for $Ph_3Ge[NHC(CH_3)CHCN]$ (**4**).

Ge(1)–C(1)	1.940(2)	C(1)–Ge(1)–C(7)	111.67(7)
Ge(1)–C(7)	1.941(2)	C(1)–Ge(1)–C(13)	110.75(7)
Ge(1)–C(13)	1.939(2)	C(7)–Ge(1)–C(13)	111.01(7)
Ge(1)–N(1)	1.866(1)	C(1)–Ge(1)–N(1)	104.97(6)
N(1)–C(19)	1.359(2)	C(7)–Ge(1)–N(1)	108.97(7)
C(19)–C(20)	1.363(2)	C(13)–Ge(1)–N(1)	109.26(7)
C(19)–C(22)	1.505(2)	Ge(1)–N(1)–C(19)	129.75(1)
C(20)–C(21)	1.416(2)	N(1)–C(19)–C(20)	123.5(2)
C(21)–N(2)	1.153(2)	N(1)–C(19)–C(22)	115.1(1)
		C(19)–C(20)–C(21)	121.6(2)
		C(20)–C(21)–N(2)	178.3(2)
		C(20)–C(19)–C(22)	121.4(2)



Scheme 2. Synthesis of 2,6-dimethyl-4-(triphenylgermylamino)pyrimidine (**5**).

angle is 121.6(1)°. Since the second substituent at the nitrogen atom in **1** is a hydrogen rather than an R_3Ge-group, it is expected that the bond length would be shorter and the N–Cα–Cβ bond angle would be more acute in the free amine. However, the structure of the lithium salt $[LiNHC(CH_3)CHCN(NC_5H_5)_2]_2$ (**6**) has been determined, and this material is a dimer in the solid state that adopts the (*Z*)-configuration about the C=C bond to allow the formation of the dimeric structure [16]. Therefore, the metric parameters within the 3-amidocrotononitrile group of this species are significantly different from those in **3** and **4**. Most notably, the N–Cα bond distance in **6** is 1.249(5) Å and the N–Cα–Cβ bond angle is 127.8(4)°. The N–Cα bond distance in **6** is shorter than those in both **3** and **4** as well as those in the free amine due to the formal negative charge located at the nitrogen atom in **6** that is absent in these three other covalently-bonded compounds.

Compound **5** was synthesized via treatment of 4-amino-2,6-dimethylaminopyrimidine with one equiv. of Bu^nLi followed by reaction with Ph_3GeCl and was isolated in 83% yield (Scheme 2). The ^1H NMR spectrum of **5** exhibits resonances at δ 5.56, 4.21, 2.36, and 2.12 ppm corresponding to the *ortho*-aromatic proton, the amide proton, the protons of the 6-methyl group, and the protons of the 2-methyl group (respectively). The resonances for the aromatic and amide protons are shifted significantly upfield from those in the free ligand (δ 6.10 and 5.29 ppm, respectively), once again due to the attachment of the nitrogen atom to germanium.

An ORTEP diagram of **5** is shown in Fig. 2 and selected bond distances and angles are collected in Table 2. The average Ge–C_{ipso} bond distance is 1.944(1) Å, the average C_{ipso}–Ge–C_{ipso} bond angle is 111.15(5)°, and the average C_{ipso}–Ge–N bond angle is 107.66(5)°, indicating a distorted tetrahedral environment at germanium that is similar to that observed in **4**. The Ge–N bond distance in **5** is 1.861(1) Å and the Ge–N–C bond angle is 121.79(7)° indicating that the geometry at nitrogen is planar in **5** and is only slightly distorted from the ideal value of 120°. The bond distances and angles within the pyrimidine ring are nearly identical to those in the free amine **2** [9]. The average N–C and C–C bond distances within the pyrimidine ring are 1.347(1) and 1.391(2) Å (respectively). The respective single and double bond distances for a N–C bond are 1.46 and 1.27 Å, while the respective single and double bond distances for a C–C bond are 1.50 and 1.35 Å [17] All of the carbon and nitrogen atoms in the pyrimidine ring are coplanar, the N–C and C–C bond distances in **5** are intermediate between the single and double bond value, and the N–C–N, N–C–C, and C–C–C bond angles within the pyrimidine ring in **5** range from 115.9(1) to 126.92(9)°. Therefore, these metric parameters indicate that the pyrimidine ring in **5** maintains its aromaticity upon attachment to germanium.

We attempted to observe the conversion of Ph_3GeCH_2CN to **4** and also **4** to **5** by NMR spectroscopy since both 3-aminocrotononitrile and 4-amino-2,6-dimethylaminopyrimidine were isolated during the attempted preparation of $(Ph_3Ge)_4Ge$ from $(Ph_3Ge)_3GeNMe_2$ and Ph_3GeH after a reaction time of 72 h [8,9]. However, no reaction was observed upon heating Ph_3GeCH_2CN in CD_3CN solvent for one week and heating **4** under the same conditions only resulted in the isomerization of the mixture of (*E*)- and (*Z*)-isomers to the more stable (*E*)-isomer while the generation of **5** was not detected. The conversion of acetonitrile and 3-aminocrotononitrile to 4-amino-2,6-dimethylaminopyrimidine in the presence of a catalytic amount of $[Me_4N][OH]\cdot 5H_2O$ has been reported and it has also been noted that heating acetonitrile for long periods of time in the presence of $[Me_4N][OH]\cdot 5H_2O$ also generates small amounts of 4-amino-2,6-dimethylaminopyrimidine [18].

The presence of a base appears necessary for the interconversion to take place in the case of both the free molecules and also when these species are employed as ligands. In the aforementioned reaction of $(Ph_3Ge)_3GeNMe_2$ and Ph_3GeH, the base present is $HNMe_2$ that is generated after the *in situ* conversion of $(Ph_3Ge)_3GeNMe_2$ to the α-germyl nitrile $(Ph_3Ge)_3GeCH_2CN$ [8,9]. The pK_a of dimethylamine is 10.64 [19] which is significantly less than that of hydroxide, but it appears that $HNMe_2$ is sufficiently basic enough to

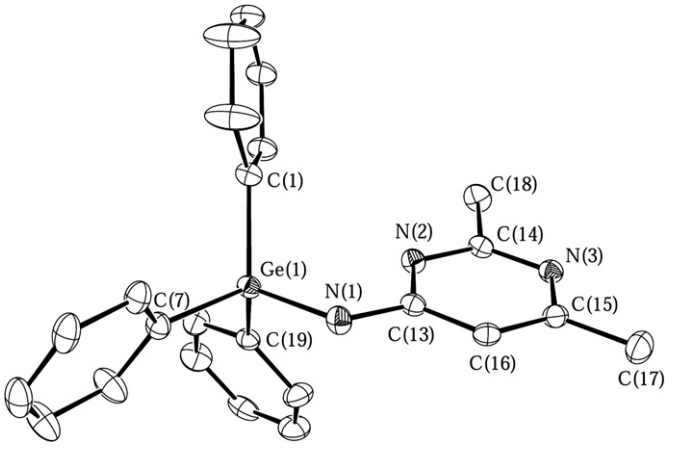


Fig. 2. ORTEP diagram of $Ph_3Ge[NHC_4N_2Me_2\text{-}2,6]$ (**5**). Thermal ellipsoids are drawn at 50% probability.

Table 2
Selected bond distances (Å) and angles (°) for 2,6-dimethyl-4-(triphenylgermylamino)pyrimidine (**5**).

Ge(1)–C(1)	1.945(1)	C(1)–Ge(1)–C(7)	113.49(5)
Ge(1)–C(7)	1.945(1)	C(1)–Ge(1)–C(19)	111.31(4)
Ge(1)–C(13)	1.943(1)	C(7)–Ge(1)–C(19)	108.66(5)
Ge(1)–N(1)	1.861(1)	C(1) –Ge(1)–N(1)	111.40(5)
N(1)–C(13)	1.357(1)	C(7)–Ge(1)–N(1)	102.75(4)
N(2)–C(13)	1.351(1)	C(13)–Ge(1)–N(1)	108.82(5)
N(2)–C(14)	1.336(1)	Ge(1)–N(1)–C(13)	121.79(7)
N(3)–C(14)	1.338(1)	N(1)–C(13)–C(16)	123.57(9)
N(3)–C(15)	1.362(1)	N(1)–C(13)–N(2)	115.8(1)
C(13)–C(16)	1.405(2)	N(2)–C(14)–N(3)	126.92(9)
C(14)–C(18)	1.505(2)	N(2)–C(13)–C(16)	120.66(9)
C(15)–C(16)	1.377(2)	N(2)–C(14)–C(18)	115.7(1)
C(15)–C(17)	1.498(2)	N(3)–C(14)–C(18)	117.36(9)
		N(3)–C(15)–C(16)	121.8(1)
		N(3)–C(15)–C(17)	116.5(1)
		C(13)–C(16)–C(15)	117.89(9)
		C(13)–N(2)–C(14)	116.81(9)
		C(14)–N(3)–C(15)	115.82(9)
		C(16)–C(15)–C(17)	121.7(1)

promote the dimerization and trimerization of acetonitrile and/or the conversion of the dimeric form to the trimeric one. In order to investigate this postulate, we monitored the reactions of both Ph_3GeCH_2CN [1] and **4** in CH_3CN solvent in the presence of $HNMe_2$ using ^1H NMR spectroscopy.

A sample of Ph_3GeCH_2CN was stirred in CH_3CN solvent at 85 °C in the presence of $HNMe_2$ and aliquots of this solution were removed at regular intervals, the volatiles were removed *in vacuo*, and the residue was taken up in C_6D_6. The ^1H NMR spectrum of an aliquot of Ph_3GeCH_2CN stirred in CH_3CN solvent at 85 °C for 18 h indicated that the conversion of Ph_3GeCH_2CN to **4** had commenced. Based on the integration of the signal at δ 1.98 ppm [1] corresponding to the α-protons of the $-CH_2CN$ ligand to that corresponding to the methyl group of the 3-amidocrotononitrile ligand of **4** at δ 1.78 ppm, ca. 20% of Ph_3GeCH_2CN had been converted to **4**. Heating for an additional 48 h resulted in ca. 65% conversion to **4**, and after 5 days none of the Ph_3GeCH_2CN remained and only signals corresponding to **4** and **5** were present. The formation of **5** was initially detected after a reaction time of 48 h, as singlets at δ 5.56, 2.36, and 2.12 ppm were clearly visible at this time in the ^1H NMR spectrum and after heating the reaction mixture at 85 °C for a total time of 9 days only the pyrimidine compound **5** was present.

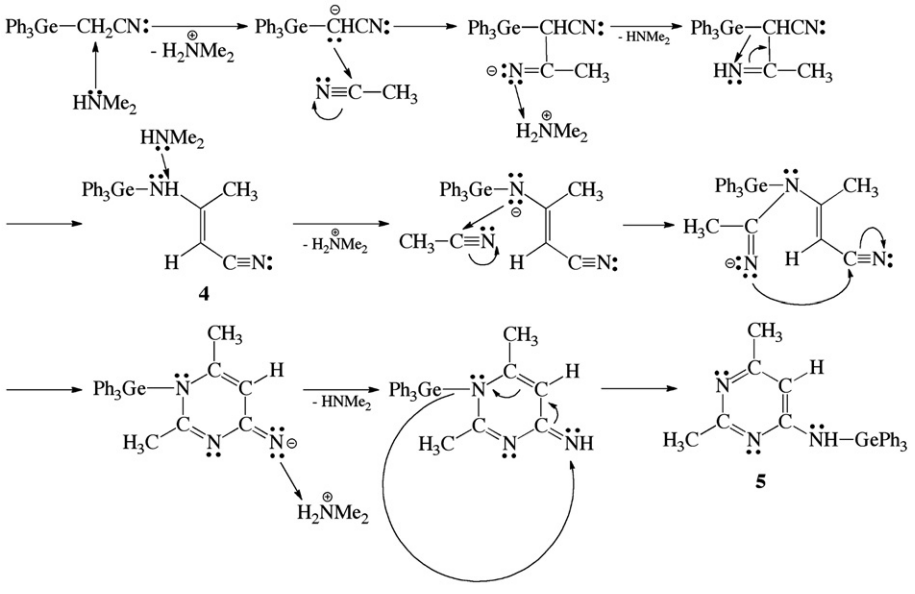
In a separate experiment, compound **4** was stirred in CH_3CN in the presence of $HNMe_2$ at 85 °C and the reaction was monitored in a similar fashion using ^1H NMR spectroscopy. In this case, the initial formation of **5** was detected after a reaction time of 6 h and complete conversion of **4** to **5** had occurred after a reaction time of 4 days. Heating of the reaction mixture for a further 7 days did not result in the detection of any additional reaction products indicating that **5** is stable with respect to additional reaction with CH_3CN. The conversion of free CH_3CN to its dimer and trimer has been reported [18], and it also is evident that this transformation can occur when the CH_3CN is bound to a metal center, in this case germanium, as the $-CH_2CN$ ligand.

The proposed pathway for the conversion of Ph_3GeCH_2CN to **4** and the subsequent transformation of **4** to **5** is shown in Scheme 3, which is consistent with the pathway that has been described for the free amines and related species [20,21]. The transformation of Ph_3GeCH_2CN to **4** involves an initial deprotonation at the α-carbon of Ph_3GeCH_2CN, and the resulting nucleophilic site attacks the cyano carbon of CH_3CN and after rearrangement the triphenylgermyl group migrates such that it becomes attached to the nitrogen atom that results from the incoming molecule of CH_3CN. The conversion of **4** to **5** is presumed to proceed via the deprotonation of the nitrogen atom located *alpha* to germanium and this nucleophilic nitrogen attacks the cyano carbon of a second CH_3CN molecule. Rearrangement of the resulting species, followed by a second attack of nitrogen on the carbon atom of the cyano group originally belonging to the 3-amidocrotononitrile ligand yields an imine that undergoes a rearrangement to provide **5**. This last rearrangement also involves another migration of the Ph_3Ge-group.

3. Conclusions

Previous investigations have suggested that the α-germyl nitrile species R_3GeCH_2CN, which are generated *in situ* from the corresponding germanium amides R_3GeNMe_2 in acetonitrile solvent, can undergo further reaction with the CH_3CN solvent to yield germanes having ligands that consist of dimeric or trimeric acetonitrile, particularly when steric crowding is present at the active germanium site. The 3-amidocrotononitrile compound $Bu^t_3Ge[NHC(CH_3)=CHCN]$ (**3**) was isolated during the attempted synthesis of $Bu^t_3GeGePh_3$ from $Bu^t_3GeNMe_2$ and Ph_3GeH, [1] and both 3-aminocrotononitrile and 2,6-dimethyl-4-aminopyrimidine were generated during the reaction of $(Ph_3Ge)_3GeNMe_2$ with Ph_3GeH [8,9]. Both of these reactions have significant steric bulk at the amide-substituted germanium center involved in the reaction, and presumably the presence of bulky substituents significantly diminishes the rate of the hydrogermolysis reaction between the germanium hydride and the α-germyl nitrile such that germanium–germanium bond formation is not observed even after prolonged reaction times. The α-germyl nitrile is generated *in situ* from the germanium amide starting material with concomitant liberation of $HNMe_2$, and the conversion of the germanium bound $-CH_2CN$ ligand first to a 3-amidocrotononitrile ligand and subsequently to the pyrimidine ligand is the only reaction that is observed with sterically encumbered germanium reagents. The presence of the base $HNMe_2$ is required for this transformation to take place.

In light of these findings, the two germanes $Ph_3Ge[NHC(CH_3)=CHCN]$ (**4**) and 2,6-dimethyl-4-(triphenylgermylamino)pyrimidine (**5**) have been prepared and structurally characterized, and their



Scheme 3. Proposed pathway for the formation of **4** and **5**.

structures have been correlated with their NMR spectra. Using ^{1}H NMR spectroscopy, it has been determined that the α-germyl nitrile Ph_3GeCH_2CN can be converted to both **4** and **5** in CH_3CN solvent at 85 °C in the presence of the base $HNMe_2$. Furthermore, the conversion of **4** to **5** was observed under the same reaction conditions. These transformations are analogous to those which have been reported for CH_3CN and $HNHC(CH_3)$═CHCN, and indicate that the oligomerization of acetonitrile can also occur when this material is bound to germanium as the $-CH_2CN$ ligand.

4. Experimental section

4.1. General considerations

All manipulations of air-sensitive compounds were carried out under an inert nitrogen atmosphere using standard Schenk, syringe, and glovebox techniques [22]. The reagents 3-aminocrotononitrile and 2,6-dimethyl-4-aminopyrimidine were purchased from Acros Organics, Ph_3GeCl was purchased from Gelest, and Bu^{n}Li (2.5 M in hexanes) was purchased from Aldrich. The compound Ph_3GeCH_2CN was prepared according to the literature procedure [1]. The Bu^{n}Li solution was titrated against menthol using phenanthroline as an indicator prior to use and all other reagents were used without further purification. Solvents were dried using a Glass Contour solvent purification system. NMR (^{1}H and ^{13}C) spectra were acquired using a Varian Gemini 2000 spectrometer and were referenced to residual protio solvent. Melting points are uncorrected. Elemental analyses were conducted by Galbraith Laboratories (Knoxville, TN).

4.2. Synthesis of $LiNHC(CH_3)CHCN$

To a solution of 3-aminocrotononitrile (2.00 g, 24.0 mmol) in THF (50 mL) was added a solution of 2.8 M Bu^{n}Li in hexane (4.3 mL, 12.0 mmol) via cannula. The resulting mixture was stirred at room temperature for 2 h and the volatiles were removed *in vacuo* to yield $LiNHC(CH_3)CHCN$ (1.90 g, 90%) as a dark brown oil.

4.3. Synthesis of $Ph_3GeNHC(CH_3)CHCN$ (**4**)

A solution of $LiNHC(CH_3)CHCN$ (0.26 g, 2.9 mmol) in THF (20 mL) was added dropwise via cannula to a solution of Ph_3GeCl (1.00 g, 2.90 mmol) in THF (30 mL) and the resulting mixture was stirred at room temperature for 2 h. The volatiles were subsequently removed *in vacuo* to yield a yellow solid that was dissolved in benzene (15 mL) and filtered through Celite. The volatiles were removed from the filtrate *in vacuo* to yield **4** (0.92 g, 80%) as a yellow solid (m.p. 126 °C). ^{1}H NMR (C_6D_6, 25 °C) (*E*)-Isomer: δ 7.55 (d, J = 7.5 Hz, 6H *o*-C_6H_5), 7.27–7.15 (m, 9H, *m*-C_6H_5 and *p*-C_6H_5), 4.06 (s, 1H, C═C*H*CN), 3.49 (s, 1H, Ge-N*H*), 1.78 (s, 3H, C*H*$_3$-C═C) ppm. (*Z*)-Isomer: δ 7.72 (d, J = 7.8 Hz, 6H *o*-C_6H_5), 7.27–7.15 (m, 9H, *m*-C_6H_5 and *p*-C_6H_5), 3.76 (s, 1H, C═C*H*CN), 3.62 (s, 1H, Ge–N*H*), 1.42 (s, 3H, C*H*$_3$–C═C) ppm. ^{13}C NMR (C_6D_6, 25 °C) (*E*)-Isomer: δ 135.2 (-*C*N), 134.5 (*ipso*-C), 134.4 (*o*-C), 130.6 (N–*C*═C), 129.8 (N–C═*C*), 128.9 (*p*-C), 128.4 (*m*-C), 69.0 (–*C*H$_3$) ppm. (*Z*)-Isomer:

Table 3
Crystallographic data for compounds $Ph_3Ge[NHC(CH_3)CHCN]$ (**4**) and $Ph_3Ge[NHC_4N_2Me_2\text{-}2,6]$ (**5**).

Compound	$Ph_3Ge[NHC(CH_3)CHCN]$ (**4**)	2,6-dimethyl-4-(triphenylgermylamino)pyrimidine (**5**)
Empirical formula	$C_{22}H_{20}GeN_2$	$C_{24}H_{23}GeN_3$
Formula weight	384.99	426.04
Temperature (K)	123(2)	123(2)
Wavelength (Å)	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/c$
a, Å	9.3073(5)	9.3920(4)
b, Å	14.1217(7)	17.6290(8)
c, Å	14.7323(8)	12.8811(6)
α, °	90	90
β, °	105.876(1)	92.118(2)
γ, °	90	90
V, Å^3	1862.5(2)	2131.3(2)
Z	4	4
ρ (g cm^{-1})	1.373	1.328
Absorption coefficient (mm^{-1})	1.650	1.451
F(000)	792	880
Crystal size (mm^3)	0.40 × 0.35 × 0.20	0.38 × 0.30 × 0.20
Theta range for data collection	2.04–25.43°	1.96–33.53°
Index ranges		
	$-10 \le h \le 11$	$-14 \le h \le 14$
	$-17 \le k \le 12$	$-27 \le k \le 27$
	$-17 \le l \le 17$	$-19 \le l \le 20$
Reflections collected	12823	54525
Independent reflections	3432 (R_{int} = 0.0294)	8344 (R_{int} = 0.0443)
Completeness to θ	θ = 25.00 (100.0%)	θ = 25.00 (100.0%)
Absorption correction	Multi-scan	Multi-scan
Max. and Min. transmission	0.686 and 0.818	0.7602 and 0.6087
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	3432/0/231	8344/0/259
Goodness-of-fit on F^2	1.053	1.051
Final R indices ($I < 2\sigma(I)$)		
R_1	0.0230	0.0279
wR_2	0.0600	0.0695
Final R indices (all data)		
R_1	0.0253	0.0349
wR_2	0.0612	0.0730
Largest diff. peak and hole (e Å^{-3})	0.465 and −0.299	0.523 and −0.465
CCDC Deposition Number	831179	831180

δ 134.8 (−*C*N), 134.5 (*ipso*-C), 134.4 (*o*-C), 130.4 (N−*C*═C), 129.1 (N−C═*C*), 128.9 (*p*-C), 128.4 (*m*-C), 67.8 (-CH_3) ppm. Anal. Calcd. for $C_{22}H_{20}GeN_2$: C, 68.61; H, 5.24. Found: C, 68.24; H, 4.90.

4.4. Synthesis of $LiNHC_4N_2Me_2$-2,6

To a solution of 2,6-dimethyl-4-aminopyrimidine (1.00 g, 9.20 mmol) in THF (50 mL) was added a solution of 2.8 M Bu^nLi in hexane (3.3 mL, 9.2 mmol) via cannula. A yellow precipitate immediately formed which redissolved after vigorous stirring. The solution was stirred at room temperature for 2 h and the volatiles were removed *in vacuo* to yield $LiNHC_4N_2Me_2$-2,6 (1.00 g, 95%) as a yellow solid.

4.5. Synthesis of 2,6-dimethyl-4-(triphenylgermylamino) pyrimidine (**5**)

A solution of $LiNHC_4N_2Me_2$-2,6 (0.400 g, 3.5 mmol) in THF (20 mL) was added dropwise via cannula to a solution of Ph_3GeCl (1.00 g, 2.9 mmol) in THF (30 mL). The solution was stirred at room temperature for 2 h and the volatiles were removed *in vacuo*. The resulting yellow solid was dissolved in benzene (15 mL) and filtered through Celite. The volatiles were removed from the filtrate *in vacuo* to yield $Ph_3Ge[NHC_4N_2Me_2$-2,6] (**5**) (1.20 g, 83%) as a yellow solid (m.p. 178 °C). ^{1}H NMR (C_6D_6, 25 °C) δ 7.68 (d, J = 7.7 Hz, 6H, *o*-C_6H_5), 7.15–7.12 (m, 9H, *p*-C_6H_5 and *m*-C_6H_5), 5.56 (s, 1H, $C_4N_2H(CH_3)_2$-2,6), 4.21 (s, 1H, Ge-N*H*), 2.36 (s, 3H, $C_4N_2H(CH_3)_2$-2,6), 2.11 (s, 3H, $C_4N_2H(CH_3)_2$-2,6) ppm. ^{13}C NMR (C_6D_6, 25 °C) δ 166.0 (C-6), 163.4 (C-4), 162.9 (C-2), 136.0 (*ipso*-C), 135.2 (*o*-C), 129.9 (*p*-C), 128.6 (*m*-C), 102.2 (C-5), 25.4 (-CH_3-2), 23.8 (-CH_3-6) ppm. Anal. Calcd. for $C_{24}H_{23}GeN_3$: C, 67.63; H, 5.44. Found: C, 67.17; H, 5.57.

4.6. Reaction of Ph_3GeCH_2CN with CH_3CN

A solution of Ph_3GeCH_2CN (0.500 g, 1.45 mmol) was dissolved in CH_3CN (30 mL) in a Schlenk tube and $HNMe_2$, which was generated by the hydrolysis of $LiNMe_2$ in a Schlenk flask, was condensed in at −78 °C. The reaction mixture was stirred at 85 °C, and aliquots were removed at regular intervals via syringe after cooling the reaction mixture to −15 °C. The volatiles were removed from these aliquots *in vacuo* and the remaining material was dissolved in benzene-d_6 (0.5 mL).

4.7. Reaction of $Ph_3GeNHC(CH_3)CHCN$ (**4**) with CH_3CN

A solution of **4** (0.45 g, 1.17 mmol) was dissolved in CH_3CN (30 mL) in a Schlenk tube and $HNMe_2$, which was generated by the hydrolysis of $LiNMe_2$ in a Schlenk flask, was condensed in at −78 °C. The reaction mixture was stirred at 85 °C, and aliquots were removed at regular intervals via syringe after cooling the reaction mixture to −15 °C. The volatiles were removed from these aliquots *in vacuo* and the remaining material was dissolved in benzene-d_6 (0.5 mL).

4.8. X-ray crystal structure analysis

X-ray crystallographic measurements for **4** and **5** were made using a Bruker APEX CCD system under a stream of nitrogen gas. Data were corrected for absorption using SADABS and the structures were solved using direct methods (SIR-2004). All non-hydrogen atoms were refined anisotropically by full-matrix least squares (SHELXL-97). Data were corrected from absorption using SADABS and all non-hydrogen atoms were refined using full-matrix least squares (SHELXL-2008). Crystallographic data for **4** and **5** are collected in Table 3. The CCDC deposition numbers shown in Table 3 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.ac.uk/data_request/cif

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