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Intermolecular C−H Insertions and Cyclization Reactions Involving a Stable Germylene

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A great deal of chemical research has focused upon C−H activation and insertion reactions in hopes of developing general methods for introducing functionality into a variety of organic molecules.[1,2] One such area of interest has been the development of insertion and activation chemistry for the α-C−H bonds in organonitriles. A number of transition and lanthanide metal-based chemistries have been previously reported.[3−13] In this paper, novel germylene-based intermolecular C−H insertions are reported for acetonitrile, phenyl acetonitrile, propionitrile, and succinonitrile. While exploring the generality of germylene insertion into the α-C−H of bond nitriles, it was discovered that adiponitrile cyclizes in a fashion reminiscent of the Thorpe−Zeigler reaction.[14,15] However, an unprecedented C−CN bond breaking step leading to the formation of a Ge−CN bond also occurs.

Although germylenes are known to insert into a variety of bonds including Si−H,[16] Ge−H,[17] and C−X bonds,[18−22] both C−H and C−C bonds are generally unreactive to germylenes. To the best of our knowledge, only two cases of germylene insertion into any type of C−H bond have been reported, both of which were intramolecular.[23−25] Jutzi demonstrated that this type of C−H insertion may be Lewis acid-catalyzed.[24] This situation is similar to that of transition metal alkane C−H activation chemistry prior to 1969 when many intramolecular “tuck-in” examples of C−H activation were known, but no intermolecular examples had yet been discovered.[26]

Bis[bis(trimethylsilyl)methyl]germylene (**1**)[27] inserts into the α-C−H bond of acetonitrile in the presence of tetrahydrofuran (THF) and LiCl, $MgCl_2$, or LiBr to yield $[(Me_3Si)_2CH]_2GeH(CH_2CN)$ (**2**) quantitatively as monitored by ^{1}H NMR spectroscopy (Scheme 1). The initially bright yellow solution faded to a clear, pale yellow color as the reaction proceeded to completion. Similar reactivity was observed for propionitrile, phenyl acetonitrile, and succinonitrile to yield $[(Me_3Si)_2CH]_2GeH[CH(CH_3)CN]$ (**3**), $[(Me_3Si)_2CH]_2GeH[CH(C_6H_5)CN]$ (**4**), and $[(Me_3Si)_2CH]_2GeH[CH(CN)CH_2CN]$ (**5**), respectively.

The presence of THF and specific salts was essential for the insertion reaction. The effect of solvent and salt has been most extensively explored for the reaction with acetonitrile. For this substrate, no reaction occurred over a 1 week period at 20 °C when benzene, diethyl ether, or 1,4-dioxane were used as solvents in the absence of added salt. However, when 0.5 mol equiv of THF was added to the reaction mixture in benzene, the reaction slowly proceeded to ~5% completion after 3 days at 20 °C as estimated by ^{1}H NMR spectroscopy. The reaction rate was also dramatically affected by added salt. In THF solvent, the reaction is complete within 2 and 20 min, respectively, if ≥ 0.2 equiv of $MgCl_2$ or LiCl are added. Upon addition of 1.0 equiv LiBr the reaction is complete in 1 h. When the reaction was run in the presence of Bu_4NCl, side reactions occurred, and only a trace of C−H insertion product was observed. Reactions run in THF without added salt exhibit variable reaction rates, from 30 min to >1 week, depending upon the batch of **1** employed. This variability in rate is likely caused by trace $MgCl_2$ impurities in the starting material.

Insertion products **2**−**5** were characterized by ^{1}H and ^{13}C NMR spectroscopy, IR and mass spectroscopies. Elemental analyses were successfully obtained for **2** and **3**. For **2**, the ^{1}H NMR spectrum shows two singlets at 0.11 and 0.13 ppm for the four sets of Si*Me*$_3$ protons and one doublet at −0.26 ppm ($^3J_{\mathrm{H-H}} = 3.2$ Hz) for the two C*H*$(SiMe_3)_2$ protons, indicating a plane of symmetry in the germane. An A_2M_2X spin system was used to simulate the Ge−*H* proton yielding a triplet of triplets centered at 4.67 ppm with ($^3J_{\mathrm{H-H}} = 2.0$ and 3.2 Hz). For **3**, four singlets at 0.074, 0.12, 0.16, and 0.26 ppm for the Si*Me*$_3$ group and two resonances at −0.23 and 0.066 ppm for the two C*H*$(SiMe_3)_2$ groups indicate the absence of a plane of symmetry. The lack of symmetry results in a ABM_3PX spin system for the Ge−*H* multiplet centered at 4.53 ppm giving a doublet of doublet of doublets ($^3J_{\mathrm{H-H}} = 1.0$, 1.6, and 4.0 Hz). The IR spectrum of **2** shows key bands at 2027 (Ge−H) and 2230 (C≡N) cm^{-1}. For **3**, IR bands at 2019 (Ge−H) and 2220 (C≡N) cm^{-1} are observed. Spectroscopic details for complexes **4** and **5** follow the same general patterns and are available with full experimental details in the Supporting Information.

The ORTEP diagram derived from the X-ray crystal structure of **2** is shown in Figure 1. The molecule sits on the 2-fold special position in the *Aba*2 space group with the rotation axis going through Ge and N1. Thus, the two $-CH(SiMe_3)_2$ groups are crystallographically equivalent, and the $-CH_2CN$ and H moieties are disordered. A 50% site occupancy was used to model both the disorder of the $-CH_2CN$ group and to calculate the Ge−H using a riding model. **2** has a roughly tetrahedral geometry with

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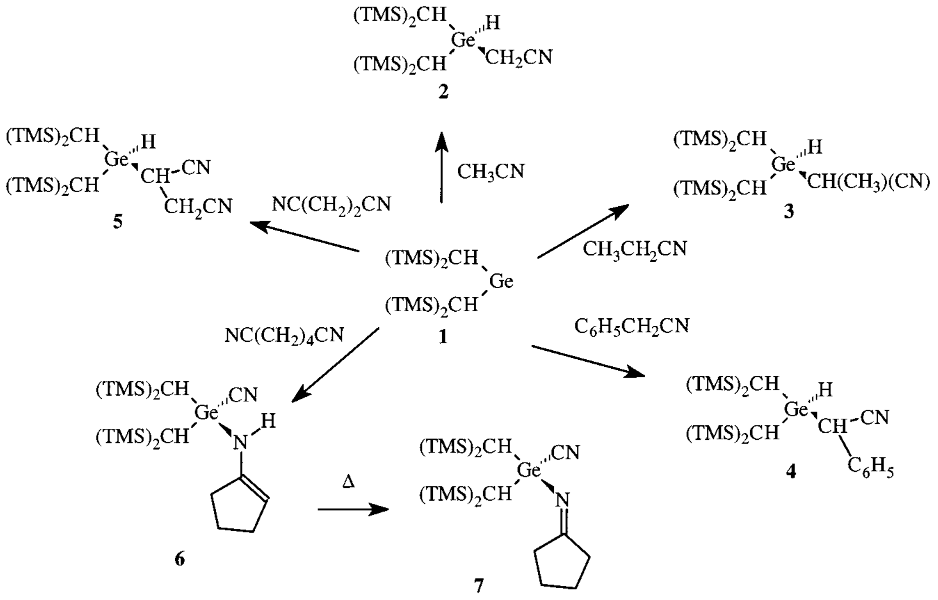
Scheme 1



a Ge−CH_2CN bond length of 1.911(9) Å and CH−Ge−CH_2CN bond angles of 121.2(3)° and 110.1(4)°.

The reaction of **1** with adiponitrile ($NC(CH_2)_4CN$) gave cyclized product **6**, bis[bis(trimethylsilyl)methyl]-cyano-*N*-(1-cyclopentenyl)amino germane. The structure of **6** was determined using ^1H and ^{13}C NMR, $^1H-^1H$ COSY, $^1H-^{13}C$ HETCOR, and IR spectroscopies as well as GC/MS. The IR spectrum shows bands at 3344 (N−H), 2192 (C≡N), and 1644 (C=C) cm^{-1}. The ^1H NMR spectrum shows two singlets at 0.20 and 0.31 ppm for the Si*Me*$_3$ protons and a singlet at −0.021 ppm for the C*H*$(SiMe_3)_2$ protons. The ring protons are accounted for by a triplet at 2.23 ppm ($^3J_{H-H} = 7.2$ Hz) for =C(N)C*H*$_2$, a quintet at 1.75 ppm ($^3J_{H-H} = 7.2$ Hz) for $CH_2CH_2CH_2$; a triplet of doublets at 2.44 ppm ($^3J_{H-H} = 2.0$ and 7.2 Hz) for =CHC*H*$_2CH_2$; and a broad singlet at 5.04 ppm corresponding to C=C*H*. The amine proton was observed as a broad singlet at 2.32 ppm. GC/MS of the hydrolysis of **6** showed formation of cyclopentanone, suggesting that the product is the germylene trapped cyclopentene cyanamide, not cyclohexeneamine. Upon sublimation at 80 °C, the N−H feature is no longer present in either the ^1H NMR or IR spectra, a new IR band assigned to C=N is observed at 1680 cm^{-1}, and the two pair of symmetric ring CH_2 groups are observed at 1.44 and 2.37 in the ^1H NMR spectrum. The new compound is assigned as the imine tautomer (**7**).

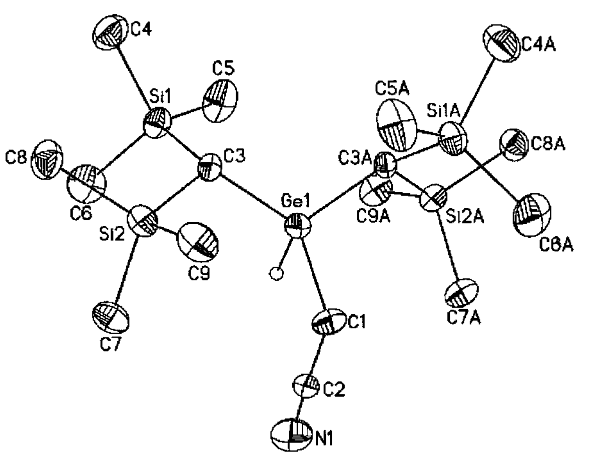


Figure 1. X-ray crystal structure of $Ge[CH(SiMe_3)_2]_2[H][CH_2CN]$ (**1**). Selected bond lengths (Å) and angles (deg): Ge−C1, 1.911(9); C1−C2, 1.443(15); C2−N1, 1.153(13); Ge−C3, 1.956(4); C1−Ge−C3, 121.2(3); C1−Ge−C3A, 110.1(4); C3−Ge−C3A, 113.9(3); Ge−C1−C2, 115.2(7); C1−C2−N1, 177(1).

Recent theoretical studies by Su and Chu have addressed the issue of germylene insertion into C−H bonds.[28] Their studies suggest insertion into C−H bonds is favored by germylenes with bulky, electropositive substituents, consistent with the observations reported in this paper. The presence of electronegative or π-donating ligands was predicted to inhibit C−H insertion reactions, and we have not observed the same C−H insertion activity for the closely related germylene $Ge[N(SiMe_3)_2]_2$. Su and Chu suggest that molecules containing unactivated C−H bonds such as methane should be susceptible to insertion reactions by germylenes. We have not observed such activity to date using stable germylenes; however, the predictions certainly provide a challenge for future work in this area. The critical role of salt observed in these reactions is reminiscent of carbenoid chemistry and suggests that mechanistic pathways for these reactions may be quite different from those explored theoretically by Su and Chu.

Intermolecular C−H insertion by a stable germylene into the α-CH bond of acetonitrile, propionitrile, phenyl acetonitrile, or succinonitrile occurs when employing THF/salt solutions under mild reaction conditions in excellent yields. Furthermore, reaction of germylene with adiponitrile results in ring closure and cleavage of a C−CN bond to yield the germanium-trapped cyclopentene cyanamide. Modification of the germylene ligand set should allow an expansion of the type of C−H bonds amenable to insertion reactions. Continued research into the mechanism of this reaction, particularly the role of salt effects, and exploration of a wider variety of substrates is planned.

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Supporting Information Available: Full experimental and spectroscopic details are provided for all compounds reported (PDF). An X-ray crystallographic file in CIF format for compound **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

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