Group 14 Elements

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The Addition of Nitriles to a Molecular Digermene: Reversible Addition and Comparison to Surface Reactivity**

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***Abstract:** The addition of acetonitrile, propionitrile, and acrylonitrile to tetramesityldigermene was investigated and compared to the addition of acetonitrile and acrylonitrile to germanium dimers on the Ge(100)-2×1 surface. In each case, a 1,2,3-azadigermetine was formed as the major product. As on the surface, the addition of nitriles to digermenes was found to be reversible, providing the first example of a reversible cycloaddition of a ditetrelene. No evidence for a six-membered cyclic ketenimine was observed as noted in the surface chemistry, suggesting that the surface ketenimine might only form between two adjacent dimers rather than on a single dimer. The comparative chemistry provides important insights that are not possible by the independent study of each system.*

For more than half a century, cycloaddition reactions have been a cornerstone in organic synthesis. Not surprisingly then, cycloadditions of the ditetrelenes and ditetrelynes are among the first reactions investigated upon the discovery of a new species of this class. These reactions continue to feature in some of the more recent exciting developments in ditetrelene and ditetrelyne chemistry, for example, the discovery of the reversible addition of ethylene to a stable distannyne[1] with implications in the area of main group catalysis,[2] or in the cycloaddition reactions of surface disilenes and digermenes with implications in microelectronics.[3]

We have long been interested in the cycloaddition reactions of the ditetrelenes of silicon and germanium. In addition to the synthesis of novel structures using this methodology,[4] we have investigated the mechanisms of the cycloadditions of aldehydes[5] and alkynes[6] to ditetrelenes. We were particularly intrigued by the report by Bent and coworkers on the chemistry of the addition of nitriles to the germanium dimers on the Ge(100)-2×1 surface at room temperature.[7,8] Interestingly, no evidence in support of a stable surface adduct was obtained when acetonitrile was added to the germanium surface. DFT calculations showed that acetonitrile forms a very weak dative bond between the nitrilic nitrogen atom and the electrophilic "down" atom of a statically buckled germanium dimer before rearranging to either a cycloadduct through the $C{\equiv}N$ bond or a ketenimine.[8] The binding energies of the $C{\equiv}N$ cycloadduct and the ketenimine were determined to be -8.1 and -18.0 kcal mol^{-1}, respectively, and the weak binding energies lead to reversible desorption of the nitrile. In general, cycloaddition reactions of ditetrelenes and ditetrelynes are irreversible under ambient conditions with only one clear exception: the aforementioned report on the reversible addition of ethylene to a distannyne.[1] A few related reversible reactions of unsaturated heavier main group compounds have also been reported.[9]

Acrylonitrile, on the other hand, reacts with the Ge(100)-2×1 surface to give stable products.[7,8] Two types of cycloadducts were proposed based on multiple internal reflection (MIR) IR data and DFT calculations: ketenimines (cyclic single-dimer adducts and/or interdimer adducts; **1a** and **1b**, respectively) and a cycloadduct between the surface dimer and the $C{=}C$ bond of acrylonitrile (**2**; Figure 1). The ratio of **1a**,**b** to **2** was estimated to be ca. 10:1. Evidence in support of cycloaddition between the $C{\equiv}N$ bond of acrylonitrile and a $Ge{=}Ge$ surface dimer was not obtained which was understandable in light of the apparent reversible desorption of the $C{\equiv}N$ cycloadduct of acetonitrile. Recently, we have reported on the addition of nitriles to tetramesityldisilene (**3**).[10] The apparent reversible addition of acetonitrile and the formation of cyclic ketenimines in the Bent study[7,8] were intriguing as we have found that simple nitriles, such as aceto- and propionitrile, add to disilene **3** through the $C{\equiv}N$ bond to give 1,2,3-azadisiletines and a linear ketenimine was only formed upon the addition of a nitrile with relatively acidic α-hydrogens, as in phenylacetonitrile. No evidence for reversibility or cyclic ketenimines was found.

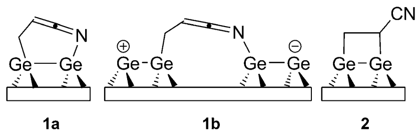

Figure 1. Acrylonitrile adducts formed on the Ge(100)-2×1 surface.

Mes$_2$Ge$=$GeMes$_2$ (**4**)[11,12] and the germanium dimers on the Ge(100)-2×1 surface often exhibit similar reactivity, for example toward carboxylic acids[12–14] and alkynes.[6c,15] Surprisingly, the reactivity of a molecular digermene toward nitriles has not yet been examined, although the reactivity of a digermyne toward benzonitrile and tetracyanoethylene has.[16] Herein, we report on the addition of various nitriles to Mes$_2$Ge$=$GeMes$_2$ (**4**) and compare the chemistry of the molecular digermene to that of the surface digermene.

The addition of excess CH_3CN, CH_3CH_2CN, or acrylonitrile to digermene **4** in THF at room temperature gave a pale

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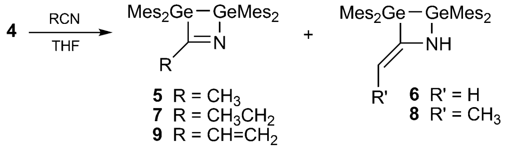
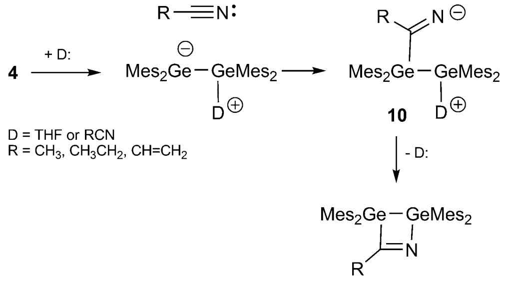
yellow solid upon removal of the solvent. ^{1}H NMR spectroscopic analysis of the crude product resulting from the addition of CH_3CN to **4** revealed the presence of 1,2,3-azadigermetine **5** with a trace of isomeric **6**. Similarly, the addition of CH_3CH_2CN to **4** produced **7** and **8** in a ratio of about 3:1, respectively. The ^{1}H NMR spectrum of the crude product of the addition of acrylonitrile to digermene **4** showed the presence of a polymeric material, likely $[Mes_2Ge]_n$, in addition to **9**. The polymer was removed by washing the crude product with hexanes. Compounds **5**–**9** decomposed upon prolonged exposure to atmospheric moisture, and therefore, were characterized promptly without purification (Scheme 1).



Scheme 1. Addition of nitriles to digermene **4**.

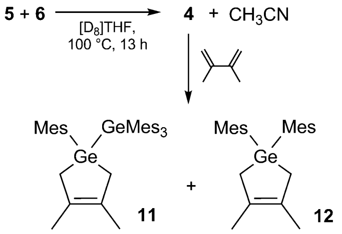
The addition of acetonitrile and propionitrile to the related disilene **3** resulted in the formation of the silicon analogues of **5**/**7** and **6**/**8**.[10] The silicon analogues of the 1,2,3-azagermetines readily rearranged to give the enamines, and thus, the stability of the azadigermetines **5** and **7** was monitored over time by ^{1}H NMR spectroscopy. In contrast to the analogous 1,2,3-azadisiletines, no increase in the relative amount of **6** or **8** was observed at room temperature, at higher temperature (100 °C) under an inert atmosphere, or upon exposure to trace amounts of atmospheric moisture.

The formation of 1,2,3-azadigermetines **5**, **7**, and **9** can be understood in terms of a formal [2+2] cycloaddition between the C≡N bond of the nitrile and the Ge=Ge bond of **4**. Given that coordination of nitriles to the buckled surface germanium dimers has been proposed as the initial step in adduct formation[8] and the cycloaddition of aldehydes to digermenes has been found to take place via an intermediate donor adduct,[5c,d] we propose that the addition of nitriles to digermene **4** begins with coordination of a donor molecule (D = THF or a molecule of nitrile) to **4** to give a zwitterionic complex (Scheme 2). Although THF or nitrile complexes of **4** have not been observed, isonitriles have been shown to form adducts with sterically protected digermynes.[17] A weak interaction between a donor molecule and **4** may be sufficient to polarize the Ge=Ge bond and initiate cyclization. After coordination of the donor molecule to the ditetrelene, the basic portion of the complex may attack the nitrilic carbon to give the zwitterionic intermediate **10**. The intermediate may then undergo intramolecular cyclization, displacing the donor molecule and forming the azadigermetine. We have proposed a similar mechanism for the formation of the analogous azadisiletines.[10] Given that we did not observe the conversion of the azadigermetines to the enamines in solution, tautomerization may take place in the intermediate **10** before cyclization to the final product.



Scheme 2. Proposed mechanism for the formation of azadigermetines.

Given the reversible desorption of CH_3CN from the Ge(100)-2 × 1 surface,[7,8] we investigated the thermal behavior of the nitrile adducts. A THF solution of **5** containing trace amounts of **6** was heated to 100 °C under an inert atmosphere. The colorless solution became bright yellow, suggesting the presence of $Mes_2Ge{=}GeMes_2$ (**4**);[11] however, the solution decolorized prior to analysis at room temperature and no major change in the composition of the mixture was observed by ^{1}H NMR spectroscopy. To determine if the yellow color of the solution was indeed due to the presence of digermene **4**, **5** was dissolved in [D_8]THF and heated to 100 °C in the presence of excess 2,3-dimethylbutadiene (DMB). The clear, colorless solution became yellow almost immediately and, after heating for ca. 13 h, a clear, colorless solution was obtained. Analysis of the crude reaction mixture by ^{1}H NMR spectroscopy revealed that **5** and **6** had been consumed. To identify the products, the volatiles were removed under vacuum to give a white solid. Analysis of the residue by ^{1}H NMR spectroscopy revealed the presence of germacyclopentenes **11**[18] and **12**[18] in a ratio of about 1.8:1 (Scheme 3).



Scheme 3. Thermolysis of **5** and **6** in the presence of DMB.

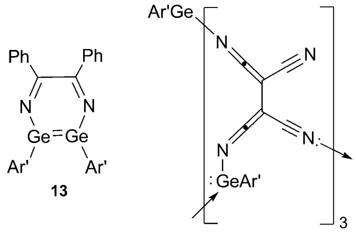
Apparently, heating **5** and **6** in THF resulted in the formation of digermene **4**, which rearranges under the conditions of the experiment to give $Mes(Mes_3Ge)Ge{:}$ which then reacts with DMB to give **11** as has been reported previously.[18] The formation of **12** was, at first, somewhat puzzling as digermene **4** has been reported to yield **11** in the presence of DMB without the formation of **12**.[12] Compound **12** is most likely formed by the reaction between $Mes_2Ge{:}$ and DMB and, presumably, is the result of expulsion of $Mes_2Ge{:}$ from the four-membered ring **5**. The formation of **11** confirms that digermene **4** is indeed produced upon heating **5** and **6**, indicating that the addition of the nitrile is indeed reversible and implying the concurrent formation of acetonitrile. Accordingly, a singlet at 1.94 ppm was observed in the ^{1}H NMR spectrum of the thermolysis reaction mixture and is assigned to CH_3CN (CH_3CN in [D_8]THF: s, 1.95 ppm).[19] Both azadigermetines **7** and **9** show similar behavior upon thermolysis in the presence of DMB.

Reversible cycloadditions are unknown in digermene chemistry, and indeed, are very rare in the chemistry of the heavier ditetrelenes and ditetrelynes. The chemistry observed here is comparable to the reversible addition of ethylene to a distannyne.[1] The reversible insertion of an isonitrile to a disilene[9a] and the reversible addition of a germylene to an alkene[9c] are notable related examples. The reversible complexation of unsaturated molecules, such as alkenes, is a key feature in the reactivity of transition metals which has led to the postulation that unsaturated main group compounds, noted primarily for their challenging syntheses and novel bonding, now have the potential of being developed into catalysts which offer several key advantages (low cost and toxicity) over their transition metal counterparts.[2] In a similar vein, Bent has postulated that the Ge(100)-2 × 1 surface may also serve as a catalyst because the buckled surface dimers exhibit donor and acceptor properties characteristic of transition-metal-based catalysts and the adsorbate–surface bonds are of an intermediate strength.[20]

The reversible addition of nitriles to digermene **4** is completely consistent with what was observed on the Ge(100) reconstructed surface for acetonitrile, albeit, the binding of the nitrile to the molecular digermene appears to be stronger than the surface digermene perhaps due to substituent effects or the different geometries at the unsaturated germaniums (*cis*-[3] versus *trans*-bent).[12] The lack of conversion of the azadigermetines to their enamine tautomers, as observed in the analogous disilene system,[10] is likely a consequence of the reversibility of the cycloaddition. Perhaps, in the digermene case, the relative amount of enamine did not increase due to competitive dissociation of the nitrile. Interestingly, we previously investigated the addition of acrylonitrile to digermene **4** at elevated temperatures and, under these conditions, no acrylonitrile adduct was isolated.[21] We now understand that an adduct was likely not observed due to the reversible binding of the nitrile to the digermene.

In contrast, the structures of adducts formed upon addition of acrylonitrile to the germanium surface dimers in comparison to the molecular digermene are different. The addition of acrylonitrile to the Ge(100)-2 × 1 surface at room temperature results in the formation of cyclic ketenimines (**1a**,**b**) and a cyano-substituted digermetane (**2**),[7] whereas we observe the formation of an azadigermetine (**9**); no evidence for ketenimine formation or cycloaddition through the C=C bond of acrylonitrile was obtained. Analysis of **9** by IR spectroscopy revealed an absorption at 1556 cm^{-1} which was assigned to the C=N stretching vibration; no such absorption was observed by MIR-IR spectroscopy of the surface adducts. DFT calculations show that both the cyclic ketenimines **1** and digermetane **2** are formed from an initial donor adduct and that **1** is the kinetic and **2** is the thermodynamic product.[8] The calculations also predict that cycloaddition through the C≡N bond of acrylonitrile would not be observed on the Ge surface, despite having a relatively low kinetic barrier, due to the weak binding energy of the adduct, and hence, a short surface lifetime.[7,8] The lack of formation of a ketenimine in the molecular system may be explained by the reaction of acrylonitrile with two adjacent surface dimers rather than a single dimer on the surface. The group of Bent showed that the formation of an interdimer cyclic ketenimine was thermodynamically more favored compared to a single intradimer adduct, although the difference was not appreciable.[8] Considering the strain associated with the incorporation of a ketenimine into a small ring, the formation of a seven-membered cyclic ketenimine (**1b**) seems more reasonable than a six-membered ketenimine (**1a**). Isolation of stable seven-membered cyclic allenes containing a Si–Si[22] or a Ge–Ge[6c] bond provides support for the formation of analogous cyclic ketenimines on the surface. In addition, seven-membered cyclic organic ketenimines exhibit a significant degree of bending (~155°) which manifests in a lowering of the ketenimine stretching frequency[23,24] as was observed in the surface cyclic ketenimine **1**[7] although the incorporation of the Ge–Ge bond within the cyclic ketenimine is expected to reduce some of the strain. Accordingly, the ketenimine stretching vibration in **1b** is not as low as in the all-carbon derivative (1954 versus 1924 cm^{-1}, respectively). The surface results suggest that azadigermetine **9** may be the kinetic product and that the isomeric cyano-substituted digermetane may be the thermodynamic product produced under equilibrium conditions. Given that digermene **4** is known to undergo conversion to Ge_3Mes_6 (with decomposition) in solution after long periods of time,[12] we have not investigated this possibility; however, using a digermene which is stable in solution for prolonged periods, this hypothesis could be tested.

Finally, it is interesting to compare the reactivity of digermene **4** with nitriles to that of a stable digermyne (Ar′GeGeAr′, Ar′ = C_6H_3-2,6-(C_6H_3-2,6-*i*Pr_2)). Digermyne Ar′GeGeAr′ reacted with benzonitrile to give the 2:1 adduct **13** and with tetracyanoethylene to give the unusual, complex cage species **14**; simple 1:1 cycloaddition adducts were not obtained (Figure 2).[16] Although the mechanisms for the formation of **13** and **14** are unknown, the authors postulated that the formation of these products likely begins with a single electron transfer and involves radicals revealing the diradical character of the digermyne. This is in contrast to the heterolytic mechanism proposed by us for the reaction of the digermenes with nitriles. A complete understanding of the differences in reactivity between these multiply bonded germanium compounds requires further investigations.



13

14

Figure 2. Nitrile adducts of a digermyne.[16]

In summary, a comparison between the addition of nitriles to molecular and surface digermenes has provided some important insights that would not be realized in two independent studies. The surface reactivity inspired the discovery of the reversible addition of nitriles to digermenes and now suggests that digermenes may be potential catalysts. The hydrolytic instability of azadigermetines **5**, **7**, and **9** hints at their enhanced reactivity and we will explore this in the future. The lack of formation of a six-membered cyclic ketenimine in the molecular system suggests that the surface ketenimine formed upon the addition of acrylonitrile is likely **1b** and not **1a**. The surface chemistry also suggests that azadigermetine **9** is the kinetic product and, under equilibrium conditions, the isomeric digermetane may be formed. We will continue to explore the comparative studies of molecular and surface digermenes in an effort to develop useful applications for this chemistry.

Keywords: digermenes · germanium · Group 14 Elements · nitriles · surface chemistry

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