Preparation of Oligogermanes via the Hydrogermolysis Reaction

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The hydrogermolysis reaction has been shown to be useful for the formation of germanium−germanium bonds. The Ge−Ge bond forming reaction involves a germanium amide and a germanium hydride and requires the use of acetonitrile as the solvent. A key factor in the formation of the Ge−Ge bond involves reaction of the germanium amide R_3GeNMe_2 with acetonitrile solvent to furnish an α-germylated nitrile R_3GeCH_2CN which contains a labile Ge−C bond. This species undergoes subsequent reaction with a germanium hydride R_3GeH to form the Ge−Ge bond. Using this method, the digermanes $Bu^n_3GeGePh_3$ and $Et_3GeGePh_3$ have been obtained and their X-ray crystal structures have been determined. The preparation of three synthons for stepwise oligogermane chain buildup, $R_2Ge(NMe_2)CH_2CH_2OEt$ (R = Et, Bu, Ph), has also been achieved. These synthons react with Ph_3GeH in CH_3CN to afford the corresponding digermanes, which in the case of R = Et and Bu undergo subsequent reaction with DIBAL-H to generate a digermane hydride. The ethyl and *n*-butyl digermane hydrides then are subsequently reacted with an additional equivalent of the appropriate synthon to produce the corresponding trigermanes, and repetition of these two steps furnishes the tetragermanes $Ph_3GeGe(R_2)Ge(R_2)Ge(R_2)CH_2CH_2OEt$ (R = Et, Bu). Thus, in this study two new series of oligomeric organogermanium species have been prepared and fully characterized.

Introduction

There is current interest in the preparation of catenated compounds of the heavier group 14 elements due to their inherent σ-delocalization[1−3] which often results in interesting and useful optical and electronic properties in these systems.[1−12] The preparation of both oligomeric and polymeric linear species has been investigated and the properties of these systems are tunable, as they rely on the number of catenated atoms in the chain as well as on the substituents attached to the element−element backbone.

The synthesis and properties of oligomeric and polymeric silicon-[13−23] and tin-containing[24−38] systems have been extensively investigated while those of the related germanium systems remain less developed. However, a variety of oligomeric organogermanes have been prepared,[4,6,7,39−62] and many of these species exhibit properties that are dependent on the number of catenated germanium atoms and/or the identity of the organic side groups.[4,6,7,11,12,63] For example, it has been shown that a series of linear permethylated oligogermanes exhibits a decreasing ionization potential as the length of the Ge−Ge chain is

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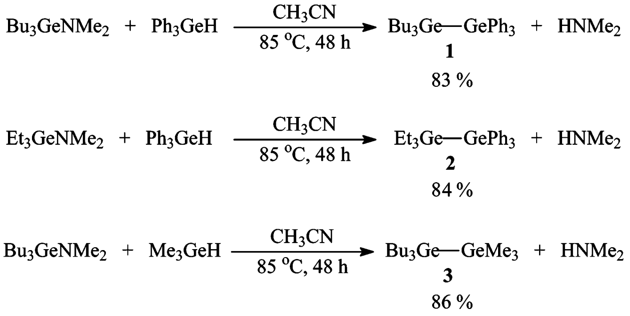
increased.[7] In a related series of perethylated oligogermanes, the position of the absorbance maximum (λ_{max}) undergoes a red shift with increasing chain length,[4] and the λ_{max} in a group of organopolygermanes also undergoes a bathochromic shift as the steric bulk of the organic side groups is increased.[6]

Traditional methods for the formation of germanium−germanium bonds include germylene insertion into a Ge−X bond (X = N, O, or a halogen), Wurtz-type coupling reactions involving organogermanium halides, reaction of organogermanium anions with organogermanium halides, reaction of organolithium or Grignard reagents with germanium halides, thermal decomposition of germylmercury compounds, and bond formation via hydrogermolysis reactions.[5,11,12,63−65] An extensive series of synthetic, spectroscopic, and structural investigations employing oligogermanes prepared by these methods was reported by Dräger *et al.*,[39−56] but most of these studies were complicated by low yields and/or the formation of mixtures of products. For example, the preparation of Ge_3Ph_8 and Ge_4Ph_{10} from $GeCl_4$ and PhMgBr resulted in a mixture of these two products which were also contaminated with Ge_2Ph_6 and $GePh_4$. This mixture required separation by HPLC giving the desired trigermane in 11% yield and the tetragermane in 18% yield.[48] The preparation of $Ph_3GeGe(Me)_2GePh_3$ resulted in similar complications.[45] Significant improvements in both product yield and selectivity have been recently achieved by the reaction of triorganogermanium halides with an excess (10 equiv) of SmI_2.[57,58]

Scheme 1



The hydrostannolysis reaction has proven very useful for the preparation of oligostannanes[8−10,38,66] but the analogous reaction is more difficult to perform in the case of germanium, typically requiring the presence of electron-withdrawing substituents on germanium to make the Ge−H bond more reactive. We are interested in obtaining a library of fully characterized oligomeric germanium systems to investigate the relationship between their structures and their properties. Additionally, such a catalog of compounds would be useful as small-molecule models for both polymeric systems and functionalized germanium surfaces bearing organic substituents. We have employed the hydrogermolysis reaction for the stepwise preparation of discrete linear oligogermanes in good to excellent yields as single molecules rather than mixtures of products, and these results are the focus of this paper.

Results and Discussion

To investigate the utility of the hydrogermolysis reaction for the formation of Ge−Ge bonds, we prepared the digermanes **1**, **2**, and **3** starting with the germanium amides $Bu^n{}_3GeNMe_2$ or Et_3GeNMe_2 as shown in Scheme 1. Initially, the synthesis of **1** was attempted at room temperature using benzene as the solvent, but no product was detected even using reaction times of up to one week. Similarly, attempts to prepare **1** in refluxing benzene or toluene were unsuccessful. However, when refluxing acetonitrile was employed as the solvent, **1** was obtained in 83% yield after 48 h.

The formation of **1**−**3** can be most easily achieved by sealing an acetonitrile solution of the reactants in a Schlenk tube and heating at 80−90 °C for 48 h, and this technique was used for the preparation of **1**, **2**, and **3**, obtained in isolated yields of 87%, 84%, and 86%, respectively (Scheme 1). These yields are generally higher than those usually obtained via other synthetic methods. For example, $Bu^t{}_3GeGeBu^t{}_3$ was isolated in 16% yield via the reduction of $Bu^t{}_3GeCl$ with lithium naphthalenide,[62] $Ph_3GeGePh_3$ was obtained in 69% yield from the reaction of PhMgBr with $GeCl_4$,[59,60] and the coupling reaction of $Bu^n{}_3GeK$ and Me_3GeCl furnished $Bu^n{}_3GeGeMe_3$ in approximately 60% yield.[67] Digermanes can be obtained from the corresponding trialkylgermanium hydrides when SmI_2 is used as the reductant in 39−96% yield, including $Et_3GeGePh_3$ which was isolated in 96% yield and $Me_3GeGeBu^n{}_3$ which was isolated in 59% yield.[57,58] This procedure thus can offer some synthetic advantages over our method when certain organic substituents are present.

The use of acetonitrile as the solvent is necessary for the success of these reactions. Germanium amides are known to react with acetonitrile resulting in α-germylated nitriles R_3-

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Scheme 2

$$\mathrm{Bu_3GeNMe_2} + \mathrm{CD_3CN} \xrightarrow[\text{- DNMe}_2]{90\ ^\circ\text{C, 1 h}} \mathrm{Bu_3GeCD_2CN} \xrightarrow[90\ ^\circ\text{C, 36 h}]{\mathrm{Ph_3GeH}} \underset{\mathbf{1}}{\mathrm{Bu_3GeGePh_3}} + \mathrm{HCD_2CN}$$

$GeCH_2CN$, which contain a reactive Ge−C bond, and bisgermylated nitriles $(R_3Ge)_2CHCN$ can also be formed as a byproduct.[68−70] The reactions are catalyzed by the addition of small amounts of Lewis acids such as $ZnCl_2$. To determine if an intermediate such as R_3GeCH_2CN plays a role in the formation of Ge−Ge bonds, the reaction of $Bu^n{}_3GeNMe_2$ with Ph_3GeH in acetonitrile-d_3 solvent was monitored by ^1H NMR spectroscopy, and the observed reaction pathway is shown in Scheme 2. Initially, a solution of $Bu^n{}_3GeNMe_2$ in CD_3CN was prepared which exhibited a sharp resonance at δ 2.45 ppm in its ^1H NMR spectrum and a peak at δ 41.5 ppm in its ^{13}C NMR spectrum arising from the amide group. After heating the sample for 1 h at 90 °C, both of these features had nearly disappeared, indicating that most of the amide had been converted to Bu_3GeCD_2CN. A resonance at δ 2.29 ppm was also clearly visible due to the formation of $DN(CH_3)_2$. At this point 1 equiv of Ph_3GeH and a small amount of Me_4Ge (ca. 5 mg as an internal standard) were added to the tube. The Ge-*H* resonance at δ 5.64 ppm was integrated versus the peak for Me_4Ge at δ 0.14 ppm to monitor the progress of the reaction. The Ge-*H* resonance at δ 5.64 ppm had decreased slightly in intensity after heating the sample for 3 h at 90 °C, and features in both the ^1H and ^{13}C NMR spectra indicated that some **1** was being formed. The progress of the reaction was monitored at regular intervals, which showed that Ph_3GeH was being continuously consumed and compound **1** was being formed. After 20 h approximately 50% of the Ph_3GeH had reacted, and after 50 h only a small amount (ca. 5%) remained. Both the ^1H and ^{13}C NMR spectra of the sample clearly indicated the clean formation of **1**.

To fully ascertain if a α-germylated nitrile is a crucial intermediate in the Ge−Ge bond forming process, we prepared Bu_3GeCH_2CN from $LiCH_2CN$ [71] and Bu_3GeCl (eq 1). The ^{13}C NMR spectrum of this species contains a broadened resonance at δ 16.0 ppm arising from the α-carbon of the $-CH_2CN$ group, while a signal for the cyano carbon appears at δ 68.1 ppm. A sample containing Bu_3GeCH_2CN and 1 equiv of Ph_3GeH in CD_3CN was prepared and the reaction was monitored by NMR spectroscopy. The initial ^1H and ^{13}C spectra taken after approximately 10 min exhibited evidence of an immediate reaction, as signals for **1** were already clearly visible. Heating the sample for 50 min at 90 °C resulted in complete consumption of Ph_3GeH and quantitative formation of **1**. Compound **1** was also obtained on a preparative scale under these conditions and was isolated in 89% yield (eq 2). The use of acetonitrile is again essential for this reaction, as Bu_3GeCH_2CN does not react with Ph_3GeH in toluene even in the presence of a catalytic amount (5 mol % based on Bu_3GeCH_2CN) of acetonitrile. Thus, the formation of an intermediate R_3GeCH_2CN species from the germanium amide and acetonitrile solvent appears to be a key factor in the success of the Ge−Ge bond formation process, and the $-CH_2CN$ moiety might thus serve as a useful functional group in future investigations.

$$\mathrm{CH_3CN} \xrightarrow[\text{THF 30 min}]{\mathrm{LiNPr^i{}_2}} \mathrm{LiCH_2CN} \xrightarrow[\substack{\text{THF, 2 h}\\ \text{- LiCl}}]{\mathrm{Bu_3GeCl}} \mathrm{Bu_3GeCH_2CN} \qquad (1)$$

$$\mathrm{Bu_3GeCH_2CN} + \mathrm{Ph_3GeH} \xrightarrow[90\ ^\circ\text{C, 50 min}]{\mathrm{CH_3CN}} \underset{\mathbf{1}}{\mathrm{Bu_3GeGePh_3}} + \mathrm{CH_3CN} \qquad (2)$$

The permutations of reactions of organotin and organogermanium hydrides and organotin and organogermanium amides were investigated in four separate ^1H NMR experiments (eqs 3−6) in order to obtain a qualitative understanding of the relative reactivities in these systems. Formation of the Sn−Sn bond was complete within 2 h (eq 3), while formation of the Ge−Sn bond using the reactants shown in eq 4 was complete within 4 h. However, complete formation of the Ge−Sn bond shown in eq 5 took 36 h, and formation of the digermane **3** required a reaction time of 48 h (eq 6). These results agree with those previously reported, which indicate that the Ge−N bond is stronger than the Sn−N bond[65,72] and that the Ge−H bond is less reactive than the Sn−H bond in reactions with species containing E−N bonds (E = Ge, Sn, Pb).[61,72−75] Thus, both of these factors result in a more sluggish reaction for the formation of Ge−Ge bonds versus reactions resulting in Sn−Sn bond formation. Additionally, the reactions involving the tin amides (eqs 3 and 5) also proceed to completion in toluene-d_8 and therefore involve hydrostannolysis of a Sn−N bond rather than a Sn−C bond.

$$\mathrm{Me_3SnNMe_2} + \mathrm{Bu_3SnH} \xrightarrow[85\ ^\circ\text{C}]{\mathrm{CH_3CN}\text{-}d_3} \mathrm{Me_3Sn{-}SnBu_3} + \mathrm{HNMe_2} \qquad (3)$$

$$\mathrm{Me_3GeNMe_2} + \mathrm{Bu_3SnH} \xrightarrow[85\ ^\circ\text{C}]{\mathrm{CH_3CN}\text{-}d_3} \mathrm{Me_3Ge{-}SnBu_3} + \mathrm{HNMe_2} \qquad (4)$$

$$\mathrm{Me_3SnNMe_2} + \mathrm{Bu_3GeH} \xrightarrow[85\ ^\circ\text{C}]{\mathrm{CH_3CN}\text{-}d_3} \mathrm{Me_3Sn{-}GeBu_3} + \mathrm{HNMe_2} \qquad (5)$$

$$\mathrm{Bu_3GeNMe_2} + \mathrm{Me_3GeH} \xrightarrow[85\ ^\circ\text{C, 48 h}]{\mathrm{CH_3CN}\text{-}d_3} \underset{\mathbf{3}}{\mathrm{Bu_3Ge{-}GeMe_3}} + \mathrm{HNMe_2} \qquad (6)$$

The X-ray crystal structures of digermanes **1** and **2** were determined and ORTEP diagrams are shown in Figures 1 and 2, while selected bond distances and angles are collected in Tables 1 and 2, respectively. Compound **1** contains two crystallographically independent molecules in the unit cell which have an average Ge−Ge distance of 2.4212(8) Å. The three phenyl and three ethyl substituents in compound **2** are symmetry related, and the Ge−Ge distance is 2.4253(7) Å. These distances can be compared to those in other linear oligogermanes including the related derivatives $Me_3GeGePh_3$, $Ph_3GeGePh_3$, and $Bu^t{}_3GeGeBu^t{}_3$, which have Ge−Ge bond lengths of 2.418(1),[76] 2.437(2),[39] and 2.710(1) Å (average between two molecules),[62] respectively. Germanium−germanium bond lengths are dependent on the size and electron-withdrawing or -donating ability of the attached organic groups, and thus both the hexaphenyl

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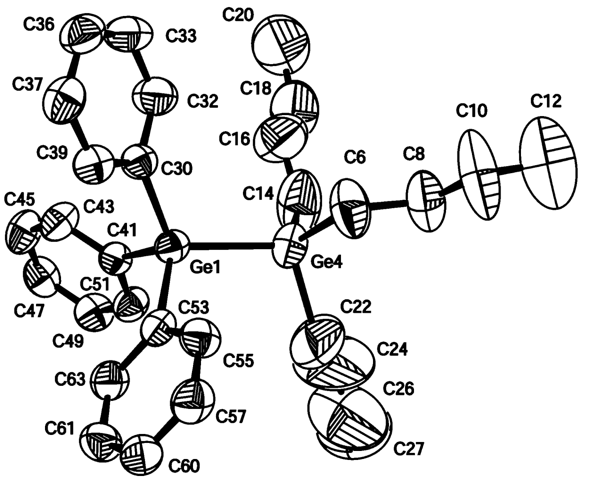

Figure 1. ORTEP diagram of one of the crystallographically independent molecules of $Bu_3GeGePh_3$ (**1a**). Thermal ellipsoids are drawn at 50% probability.

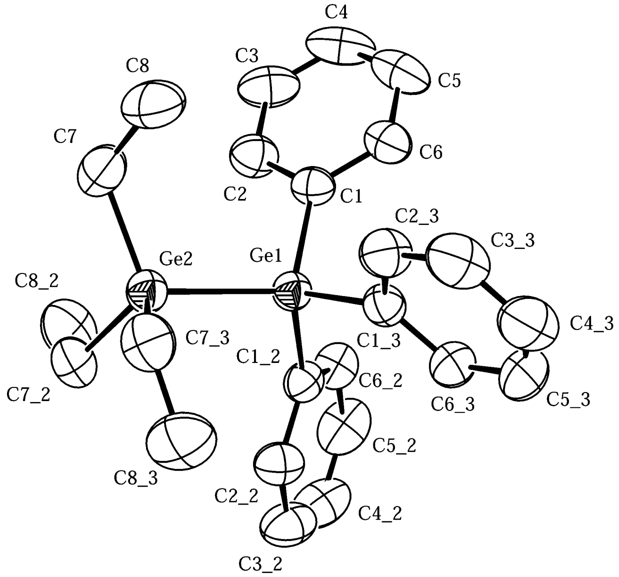

Figure 2. ORTEP diagram of $Et_3GeGePh_3$ (**2**). Thermal ellipsoids are drawn at 50% probability.

Table 1. Selected Bond Distances (Å) and Angles (deg) for the Two Crystallographically Independent Molecules of $Bu_3GeGePh_3$ (1)

1a		**1b**		average
Ge(1)−Ge(2)	2.415(8)	Ge(1′)−Ge(2′)	2.4270(8)	2.4212(8)
Ge(1)−C(21)	1.956(4)	Ge(1′)−C(21′)	1.954(4)	1.955(4)
Ge(1)−C(31)	1.956(4)	Ge(1′)−C(31′)	1.955(4)	1.956(4)
Ge(1)−C(41)	1.953(4)	Ge(1′)−C(41′)	1.952(4)	1.953(4)
Ge(2)−C(1)	1.921(5)	Ge(2′)−C(1′)	1.947(4)	1.934(4)
Ge(2)−C(5)	1.902(5)	Ge(2′)−C(5′)	1.941(5)	1.922(5)
Ge(2)−C(9)	2.006(7)	Ge(2′)−C(9′)	1.987(6)	1.997(6)
C(21)−Ge(1)−C(31)	107.2(2)	C(21′)−Ge(1′)−C(31′)	106.8(2)	107.0(2)
C(21)−Ge(1)−C(41)	107.8(2)	C(21′)−Ge(1′)−C(41′)	108.5(2)	108.2(2)
C(31)−Ge(1)−C(41)	108.3(2)	C(31′)−Ge(1′)−C(41′)	106.9(2)	107.6(2)
C(21)−Ge(1)−Ge(2)	115.0(1)	C(21′)−Ge(1′)−Ge(2′)	111.7(1)	113.4(1)
C(31)−Ge(1)−Ge(2)	111.3(1)	C(31′)−Ge(1′)−Ge(2′)	110.3(1)	110.8(1)
C(41)−Ge(1)−Ge(2)	107.1(1)	C(41′)−Ge(1′)−Ge(2′)	112.3(1)	109.7(1)
C(1)−Ge(2)−C(5)	113.8(3)	C(1′)−Ge(2′)−C(5′)	109.9(2)	111.9(2)
C(1)−Ge(2)−C(9)	105.9(3)	C(1′)−Ge(2′)−C(9′)	106.8(2)	106.4(2)
C(5)−Ge(2)−C(9)	107.3(4)	C(5′)−Ge(2′)−C(9′)	107.5(3)	107.4(3)
C(1)−Ge(2)−Ge(1)	110.0(2)	C(1′)−Ge(2′)−Ge(1′)	108.9(1)	109.5(1)
C(5)−Ge(2)−Ge(1)	112.5(2)	C(5′)−Ge(2′)−Ge(1′)	112.3(1)	112.4(1)
C(9)−Ge(2)−Ge(1)	106.9(2)	C(9′)−Ge(2′)−Ge(1′)	111.3(2)	109.1(2)

Table 2. Selected Bond Distances (Å) and Angles (deg) for $Et_3GeGePh_3$ (2)

Ge(1)−Ge(2)	2.4253(7)
Ge(1)−C(1)	1.954(2)
Ge(2)−C(7)	1.959(2)
C(1)−Ge(1)−C(1_2)	107.78(7)
C(7)−Ge(2)−C(7_2)	109.75(9)
C(1)−Ge(1)−Ge(2)	111.11(7)
Ge(1)−Ge(2)−C(7)	109.19(9)

and hexa-*tert*-butyl derivatives are expected to exhibit longer Ge−Ge bonds compared to $Me_3GeGePh_3$ and compounds **1** and **2** due to the presence of the more bulky Ph or Bu^t ligands. The alkyl substituents in the three latter species all have the same relative size and electron-donating characteristics and thus all three digermanes exhibit similar Ge−Ge bond distances, as expected.

To systematically construct chains of germanium atoms, we prepared the three synthons **5a**−**c** in good overall yields via the three-step process shown in Scheme 3. Monochlorination of the germanium dihydride reagents R_2GeH_2 proceeded in high yield.[77] These R_2GeHCl reagents were used to hydrogermylate ethyl vinyl ether to yield the chlorides **4a**−**c**, which were subsequently reacted with $LiNMe_2$ to give the amide synthons **5a**−**c**. The overall yields for the germanium amides relative to the starting materials R_2GeHCl are 82% (**5a**), 75% (**5b**), and 57% (**5c**), and the protons of the $-NMe_2$ groups of these products exhibit characteristic ^1H NMR features at δ 2.57 ppm (**5a**), δ 2.60 ppm (**5b**), and δ 2.78 ppm (**5c**). The disappearance of these resonances can be used to monitor the progress of subsequent reactions using ^1H NMR spectroscopy.

Germanes **5a**−**c** were each reacted with a slight excess of Ph_3GeH in a sealed Schlenk tube using acetonitrile as the solvent over 48 h at 90 °C to furnish the digermanes **6a**−**c** in yields of 75% (**6a**), 76% (**6b**), and 92% (**6c**) after purification by Kugelrohr distillation to remove any unreacted Ph_3GeH (Scheme 4). Care must be taken when purifying **6a** in this fashion, as it is substantially more volatile than **6b** or **6c** and can codistill with the Ph_3GeH. These digermanes have been characterized by NMR (^1H and ^{13}C) spectroscopy and elemental analysis. The ^1H NMR spectrum of **6a** exhibits a triplet at δ 3.44 ppm (J = 7.8 Hz) and a quartet at δ 3.14 ppm (J = 6.9 Hz) arising from the protons of the methylene groups bound to the oxygen atom of the ethoxyethyl substituent. For **6b** and **6c** these protons give rise to triplets at δ 3.51 ppm (J = 7.2 Hz) (**6b**) and δ 3.59 ppm (J = 7.8 Hz) (**6c**) and quartets at δ 3.18 ppm (J = 7.2 Hz) (**6b**) and δ 3.03 ppm (J = 6.9 Hz) (**6c**).

In a method similar to that used by Sita for the related tin species,[8] compounds **6a** and **6b** could be converted to the hydride-terminated digermanes **7a** and **7b** by reaction with di-*iso*butylaluminum hydride (DIBAL-H), but more vigorous reaction conditions were required in the case of germanium. Although oligostannanes can be converted to the corresponding hydrides at room temperature in ca. 1 h,[8] using this reagent for the preparation of the germanium hydrides in benzene required a reflux period of 12 h. To obtain the hydrides in pure form, the crude product mixtures were passed through a short silica gel column using benzene as the eluent in order to remove any aluminum-containing byproducts. Often subsequent distillation was required to fully remove these contaminants. In addition, the phenyl derivative **6c** could not be converted to the corresponding hydride **7c** using DIBAL-H presumably due to steric interactions between the phenyl substituents on the digermane and the isobutyl groups of $Bu^i{}_2AlH$. The yields of

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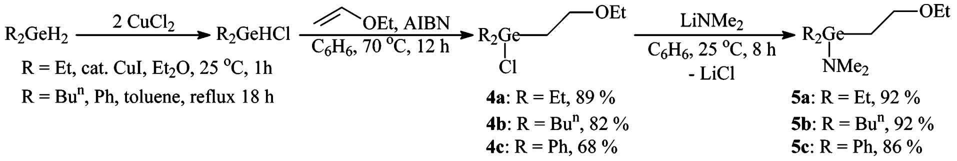
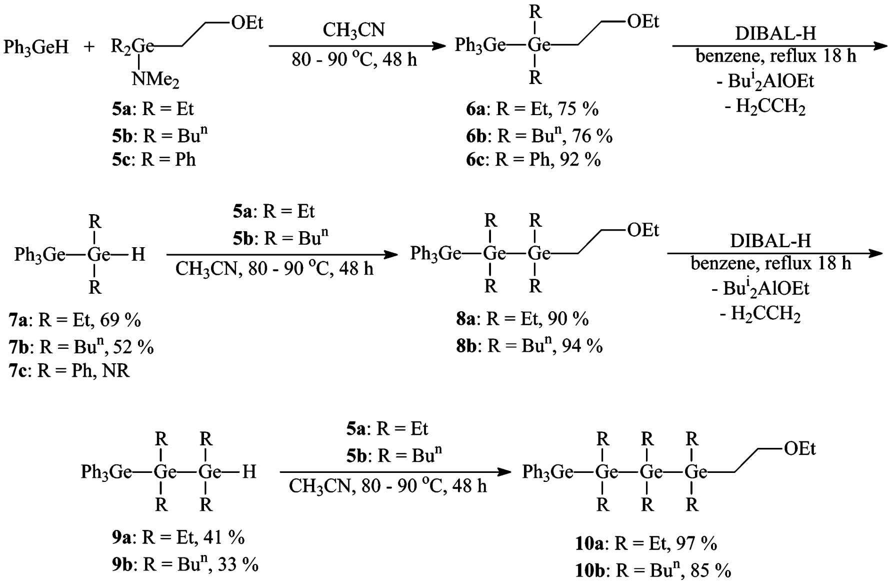
[77] Ohshita, J.; Toyoshima, Y.; Iwata, A.; Tang, H.; Kunai, A. *Chem. Lett.* **2001**, 886−887.

Scheme 3



Scheme 4



7a (69%) and **7b** (52%) are moderate, and we have attempted to circumvent this difficulty by employing $LiBH_4$ or $LiBHEt_3$ as the hydride transfer reagent. However, neither of these reagents served for the preparation of **7a**−**c** under various experimental conditions including refluxing in benzene, toluene, or THF for 48 h.

The hydrides **7a** and **7b** exhibit characteristic Ge−H stretching bands at 1996 cm^{-1} (**7a**) and 2036 cm^{-1} (**7b**) in their infrared spectra similar to other digermane hydrides.[78] They also exhibit a pentet in their ^1H NMR spectra arising from the terminal hydride at δ 4.91 ppm ($J = 3.0$ Hz) (**7a**) and δ 4.40 ppm ($J = 3.6$ Hz) (**7b**), which is broadened in each case due to coupling with the highly quadupolar ^{73}Ge nucleus. The complete conversion of the starting digermanes **6a** and **6b** to the hydrides **7a** and **7b** is indicated by the absence of the methylene features of the ethoxyethyl groups described above.

Compounds **7a** and **7b** were reacted with an additional equivalent of the corresponding germanium amides **5a** or **5b** to provide the trigermanes **8a** and **8b** in respective yields of 90% and 94% (Scheme 4), which were also characterized by NMR (^1H and ^{13}C) spectroscopy and elemental analysis. The ^1H NMR spectrum of **8a** exhibits characteristic features at δ 3.28 ppm (t, $J = 6.6$ Hz) and δ 3.14 ppm (q, $J = 6.9$ Hz) for the protons of the methylene groups bound to oxygen in the ethoxyethyl substituent, while for **8b** these features appear at δ 3.51 ppm (t, $J = 7.5$ Hz) and δ 3.18 ppm (q, $J = 6.9$ Hz). The chemical shifts of these resonances are similar to those of the digermanes **6a** and **6b**.

The composition of the products can be confirmed by integration of the aromatic versus the alkyl region in the ^1H NMR spectra of both **6a**,**b** and **8a**,**b**. For each class of compound, the alkyl region includes resonances for all protons contained in the ethyl or butyl side groups as well as the terminal methyl group and the α-methylene group of the ethoxyethyl substituent. The integrated ratio of the alkyl versus the aromatic regions of the ^1H NMR spectra of **6a** is almost exactly 1:1 as expected, while that of **8a** is 1.61:1, which is close to the predicted value of 1.67:1. A similar result was found for **6b** (1.57:1, calculated 1.53:1) and **8b** (2.80:1, calculated 2.73:1). Product compositions also were confirmed by ^{13}C NMR spectroscopy and by elemental analysis.

The trigermanes **8a** and **8b** were converted to the corresponding hydrides **9a** and **9b** again in modest yields (**9a**, 41%; **9b**, 33%), as shown in Scheme 4 and exhibit characteristic infrared ($\nu_{Ge-H} = 1996$ cm^{-1} (**9a**), 2000 cm^{-1} (**9b**)) and ^1H NMR (δ 4.31 ppm ($J = 3.2$ Hz) (**9a**), δ 4.91 ppm ($J = 3.0$ Hz) (**9b**)) spectral features. Purification of these species required first washing the crude products on a short silica column followed by vacuum distillation of the resulting material. Washing on a second silica column was required to obtain **9a** and **9b** in pure form (as shown by ^1H NMR spectroscopy) and this extensive purification is likely the cause of the diminished yields of these products. The hydrides **9a** and **9b** were subsequently employed for the preparation of the tetragermanes **10a** and **10b** in yields of 97% and 85% (Scheme 4), respectively, and the identities of these compounds were again confirmed by integration of their ^1H NMR spectra, giving alkyl:aromatic ratios of 2.32:1 for **10a** (calculated value 2.33:1) and 3.99:1 for **10b** (calculated value 3.93:1). Both tetragermanes were further characterized by ^{13}C NMR spectroscopy and elemental analysis.

The overall yields of the tri- and tetragermanes can be improved if the intermediate hydrides are not isolated but rather reacted directly with additional equivalents of the germanium amides **5**. For example, reaction of the trigermane **8b** with a slight excess of DIBAL-H in refluxing benzene for 12 h followed by removal of the solvent and treatment of the resulting crude product with 1 equiv of **5b** in CH_3CN produced the

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[78] Marchand, A.; Gerval, P. *J. Organomet. Chem.* **1978**, *162*, 365−387.

tetragermane **10b** in 75% yield, a substantial improvement over the 28% overall yield achieved when the hydride **9b** was isolated and purified. Excess DIBAL-H and the byproducts formed in the hydride transfer reaction do not interfere with the hydrogermolysis reaction, and this method thus could be useful for extension of the Ge−Ge chain length beyond four germanium atoms.

The tetragermanes **10a** and **10b** exhibit observable absorbance maxima in their electronic spectra that appear as shoulders on the CH_3CN solvent peak at 235 nm (**10a**) and 241 nm (**10b**) arising from the $\sigma \rightarrow \sigma^*$ transition. The related spectra for the di- (**6a**,**b**) and trigermanes (**8a**,**b**) as well as their respective hydrides must have absorbance maxima that are not observed above the solvent cutoff. The positions of λ_{max} for **10a** and **10b** are similar to those of other related species including the tetragermane $Et_3Ge(GeEt_2)_2GeEt_3$ (λ_{max} = 234 nm) and the hexagermane $Et_3Ge(GeEt_2)_4GeEt_3$ (λ_{max} = 258 nm).[4] The related tin-containing congeners exhibit a more substantial red shift of their absorbance maxima, as illustrated for the related tetrastannane $Bu_3Sn(SnBu_2)_2SnOCH_2CH_2OEt$, which has a λ_{max} at ca. 275 nm, and the hexastannane $Bu_3Sn(SnBu_2)_4SnCH_2CH_2$-OEt, which exhibits a λ_{max} at 310 nm.[8] The absorbance maxima for related polygermanes[79−83] such as poly(phenylmethyl)-germane (M_w = 6900, λ_{max} = 330 nm)[82] or poly(dibutyl)-germane (M_w = 14000, λ_{max} = 325 nm)[79] are also not as significantly red shifted as their shorter-chain oligostannane analogues. Further investigations are required to ascertain the reason for this difference, although these data suggest that the $\sigma \rightarrow \sigma^*$ transition in oligostannanes occurs at a lower energy than that of the germanium derivatives.

In conclusion, we have prepared and characterized two series of oligogermanes by sequential chain buildup and have used germanium amides and germanium hydrides for the formation of Ge−Ge bonds. This reaction requires the use of acetonitrile as the solvent and proceeds via the hydrogermolysis of a reactive α-germylated nitrile intermediate. The methods used in this study offer several advantages over previously employed synthetic techniques including generally improved yields, the formation of discrete molecules rather than product mixtures, and direct control over the substituents attached to the Ge−Ge backbone since the germanium atoms are added one at a time. This method therefore will facilitate the preparation of oligomers with diverse substitution patterns, which in turn permits the tailoring of molecules that might exhibit certain optical and electronic properties.

Experimental Section

General Considerations. All manipulations were carried out under an inert atmosphere using standard Schlenk, glovebox, and syringe techniques.[84] Solvents were dried using a Glass Contour solvent purification system. The starting materials Et_3GeCl, Bu_3GeCl, and Me_3GeH were purchased from Gelest and ethyl vinyl ether, AIBN, Ph_3GeH, and $LiNMe_2$ were purchased from Aldrich and used without further purification. The hydrochlorides R_2GeHCl were prepared via the method of Kunai *et al.*[77] The compounds Et_3GeNMe_2,[85] Bu_3GeNMe_2,[86] $Bu_3GeGePh_3$,[78,87,88] $Et_3GeGePh_3$,[78,88,89] and $Bu_3GeGeMe_3$[87] have been reported but were not fully characterized, and their complete characterization is described below. NMR spectra were recorded using a Varian Gemini 2000 instrument operating at 300 MHz (^1H) or 75.5 MHz (^{13}C) and are referenced to the solvent resonances. Infrared spectra were recorded using a Perkin-Elmer 2000 FTIR system. UV/visible spectra were obtained using a Hewlett-Packard Agilent UV/visible spectroscopy system. Elemental analyses were conducted by Desert Analytics.

Synthesis of Et_3GeNMe_2. A flask was charged with Et_3GeCl (2.302 g, 11.79 mmol) dissolved in benzene (30 mL). To this was added solid $LiNMe_2$ (0.789 g, 15.5 mmol). The resulting suspension was stirred for 12 h and then filtered through Celite to yield a clear solution. The volatiles were removed *in vacuo* to yield a slightly turbid oil, which was distilled using a Kugelrohr oven (oven temp = 100 °C at 0.11 Torr) to yield Et_3GeNMe_2 (1.371 g, 57%) as a clear oil. ^1H NMR (C_6D_6, 25 °C): δ 2.58 (s, 6H, GeN(CH_3)$_2$), 1.07 (t, J = 8.4 Hz, 9H, $GeCH_2CH_3$), 0.80 (m, J = 8.4 Hz, 6H, $GeCH_2$-CH_3) ppm. ^{13}C NMR (C_6D_6, 25 °C): δ 41.4 ($-N(CH_3)_2$), 9.3 ($Ge(CH_2CH_3)_3$), 4.6 ($Ge(CH_2CH_3)_3$) ppm.

Synthesis of Bu_3GeNMe_2. A flask was charged with 1.583 g (5.666 mmol) of Bu_3GeCl dissolved in benzene (30 mL). To this was added solid $LiNMe_2$ (0.354 g, 6.94 mmol). The resulting suspension was stirred for 12 h and then filtered through Celite to yield a clear solution. The volatiles were removed *in vacuo* to yield a slightly turbid oil, which was distilled using a Kugelrohr oven (oven temp = 105 °C at 0.09 Torr) to yield Bu_3GeNMe_2 (1.469 g, 90%) as a clear oil. ^1H NMR (C_6D_6, 25 °C): δ 2.62 (s, 6H, GeN(CH_3)$_2$), 1.52−1.30 (m, 12H, $GeCH_2CH_2CH_2CH_3$), 0.93 (t, J = 7.2 Hz, 9H, $GeCH_2CH_2CH_2CH_3$), 0.89 (m, 6H, $GeCH_2$) ppm. ^{13}C NMR (C_6D_6, 25 °C): δ 41.5 ($-N(CH_3)_2$), 27.4, 26.9, 14.1 (butyl group carbons), 13.2 ($-CH_2CH_2CH_2CH_3$) ppm. Anal. Calcd for $C_{14}H_{33}GeN$: C, 58.38; H, 11.55. Found: C, 58.28; H, 11.79.

Synthesis of $Bu_3Ge{-}GePh_3$ (1). A flask was charged with 0.770 g (2.67 mmol) of Bu_3GeNMe_2, which was dissolved in acetonitrile (15 mL). To this was added a solution of Ph_3GeH (0.864 g, 2.83 mmol) in acetonitrile (10 mL). The resulting solution was refluxed under N_2 for 48 h and allowed to cool, and the volatiles were removed *in vacuo*. Kugelrohr distillation (oven temp = 180 °C at 0.10 Torr) of the crude material to remove excess Ph_3GeH yielded **1** (1.21 g, 83%) as a white solid. ^1H NMR (C_6D_6, 25 °C): δ 7.72−7.64 (m, 6H, *meta*-H), 7.24−7.16 (m, 9H, *ortho*-H and *para*-H), 1.52−1.39 (m, 6H, $GeCH_2$), 1.27 (sext, J = 7.8 Hz, 6H, $GeCH_2$-$CH_2CH_2CH_3$), 1.21−1.15 (m, 6H, $GeCH_2CH_2CH_2CH_3$), 0.81 (t, J = 6.9 Hz, 9H, $GeCH_2CH_2CH_2CH_3$) ppm. ^{13}C NMR (C_6D_6, 25 °C): δ 139.7, 135.7, 128.7, 128.6 (aromatic carbons), 28.8, 26.8, 14.5, 13.8 (butyl group carbons) ppm. Anal. Calcd for $C_{30}H_{42}Ge_2$: C, 65.77; H, 7.73. Found: C, 65.74; H, 7.80.

Synthesis of $Et_3Ge{-}GePh_3$ (2). To a solution of Et_3GeNMe_2 (0.417 g, 2.00 mmol) in acetonitrile (15 mL) in a Schlenk tube was added Ph_3GeH (0.0.637 g, 2.10 mmol) in acetonitrile (15 mL). The tube was sealed with a Teflon plug, and the reaction was heated at 85 °C for 48 h. The solution was transferred to a Schlenk flask, and the volatiles were removed *in vacuo*. The crude product was distilled in a Kugelrohr oven (oven temp = 100 °C, P = 0.05 Torr) to remove excess Ph_3GeH to yield **2** as a white solid (0.247 g, 84%). ^1H NMR (C_6D_6, 25 °C): δ 7.64−7.61 (m, 6H, *meta*-H), 7.23−7.16 (m, 9 H, *ortho*-H and *para*-H), 1.03 (m, 15H, $Ge(CH_2CH_3)_3$) ppm. ^{13}C NMR (C_6D_6, 25 °C): δ 139.2, 135.6, 128.7,

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128.6 (aromatic carbons), 10.2, 6.1 (ethyl group carbons) ppm. Anal. Calcd for $C_{24}H_{30}Ge_2$: C, 62.16; H, 6.52. Found: C, 61.96; H, 6.61.

Synthesis of $Bu_3Ge-GeMe_3$ (3). A solution of Me_3GeH (0.113 g, 0.952 mmol) in acetonitrile (10 mL) was added to a solution of Bu_3GeNMe_2 (0.226 g, 0.785 mmol) in acetonitrile (10 mL) in a Schlenk tube. The tube was sealed with a Teflon plug, and the reaction mixture was heated to 85 °C for 48 h. The solution was transferred to a Schlenk flask, and the volatiles were removed *in vacuo*. The crude product was distilled in a Kugelrohr oven (oven temp = 85 °C, P = 0.05 Torr) to remove excess staring material to yield **3** as a colorless oil (0.244 g, 86%). ^1H NMR (C_6D_6, 25 °C): δ 1.58−1.51 (m, 6H, $GeCH_2CH_2CH_2CH_2CH_3$), 1.42 (pent, J = 5.7 Hz, 6H, $GeCH_2CH_2CH_2CH_3$), 0.96 (m, 15H, $GeCH_2CH_2CH_2CH_3$ and $GeCH_2CH_2CH_2CH_3$), 0.26 (s, 9H, $GeCH_3$) ppm. ^{13}C NMR (C_6D_6, 25 °C): δ 27.0, 26.8, 18.2, 14.0 (butyl groups), 1.4 ($GeCH_3$) ppm. Anal. Calcd for $C_{15}H_{36}Ge_2$: C, 49.81; H, 10.03. Found: C, 50.11; H, 10.08.

Synthesis of $Et_2Ge(Cl)CH_2CH_2OEt$ (4a). To a solution of Et_2GeHCl (1.90 g, 11.4 mmol) in benzene (30 mL) in a Schlenk tube was added ethyl vinyl ether (1.35 mL, 13.7 mmol) via syringe. A solution of AIBN (0.038 g, 0.23 mmol) in benzene (2 mL) was added to the reaction mixture. The tube was sealed with a Teflon plug and heated at 85 °C for 18 h. The solution was transferred to a Schlenk flask, and the volatiles were removed *in vacuo* to yield 2.41 g (89%) of **4a** as a clear oil. ^1H NMR (C_6D_6, 25 °C): δ 3.33 (t, J = 6.6 Hz, 2H, $-GeCH_2CH_2O$), 3.10 (q, J = 7.2 Hz, 2H, $-OCH_2CH_3$), 1.41 (t, J = 7.2 Hz, 3H, $-OCH_2CH_3$), 1.16−1.04 (m, 6H, $(CH_3CH_2)_2Ge$ and $GeCH_2CH_2O-$), 0.97 (t, J = 6.6 Hz, 6H, $Ge(CH_2CH_3)_2$) ppm. ^{13}C NMR (C_6D_6, 25 °C): δ 66.8 ($-OCH_2CH_3$), 66.0 ($GeCH_2CH_2O-$), 20.2, 15.2, 12.1, 8.2 (aliphatic carbons) ppm. Anal. Calcd for $C_8H_{19}ClGeO$: C, 40.15; H, 8.00. Found: C, 39.25; H, 8.10.

Synthesis of $Bu_2Ge(Cl)CH_2CH_2OEt$ (4b). To a solution of Bu_2GeHCl (1.28 g, 5.74 mmol) in benzene (20 mL) in a Schlenk tube was added ethyl vinyl ether (1.00 mL, 10.2 mmol) via syringe. A solution of AIBN (0.016 g, 0.097 mmol) in benzene (4 mL) was added to the reaction mixture. The tube was sealed with a Teflon plug and heated at 85 °C for 18 h. The solution was transferred to a Schlenk flask, and the volatiles were removed *in vacuo* to yield 1.40 g (82%) of **4b** as a clear oil. ^1H NMR (C_6D_6, 25 °C): δ 3.41 (t, J = 7.2 Hz, 2H, $-GeCH_2CH_2O$), 3.15 (q, J = 6.9 Hz, 2H, $-OCH_2CH_3$), 1.58−1.49 (m, 4H, $GeCH_2CH_2CH_2CH_3$), 1.47 (t, J = 6.9 Hz, 4H, $GeCH_2CH_2CH_2CH_3$), 1.32 (sext, J = 7.2 Hz, 4H, $GeCH_2CH_2CH_2CH_3$) 1.17−1.11 (m, 2H, $GeCH_2CH_2O-$), 1.01 (t, J = 6.9 Hz, 3H, $-OCH_2CH_3$), 0.89 (t, J = 7.2 Hz, 6H, $GeCH_2CH_2CH_2CH_3$) ppm. ^{13}C NMR (C_6D_6, 25 °C): δ 66.9 ($-OCH_2CH_3$), 66.1 ($GeCH_2CH_2O-$), 26.6, 26.1, 21.1, 20.0, 15.3, 13.8 (aliphatic carbons) ppm. Anal. Calcd for $C_{12}H_{27}ClGeO$: C, 48.79; H, 9.21. Found: C, 48.13; H, 8.74.

Synthesis of $Ph_2Ge(Cl)CH_2CH_2OEt$ (4c). To a solution of Ph_2GeHCl (0.590 g, 1.82 mmol) in benzene (15 mL) in a Schlenk tube was added ethyl vinyl ether (0.20 mL, 2.0 mmol) via syringe. A solution of AIBN (0.0090 g, 0.055 mmol) in benzene (2 mL) was added to the reaction mixture. The tube was sealed with a Teflon plug and heated at 85 °C for 24 h. The solution was transferred to a Schlenk flask, and the volatiles were removed *in vacuo* to yield 0.493 g (66%) of **4c** as a clear oil. ^1H NMR (C_6D_6, 25 °C): δ 7.64−7.61 (m, 4H, *meta*-H), 7.18−7.07 (m, 6H, *ortho*-H and *para*-H), 3.58 (t, J = 7.5 Hz, 2H, $-GeCH_2CH_2O$), 3.10 (q, J = 7.2 Hz, 2H, $-OCH_2CH_3$), 1.90 (t, J = 7.5 Hz, 2H, $GeCH_2CH_2O-$), 1.00 (t, J = 7.2 Hz, 3H, $-OCH_2CH_3$) ppm. ^{13}C NMR (C_6D_6, 25 °C): δ 136.7, 134.0, 130.2, 128.5 (aromatic carbons), 66.1 ($-OCH_2CH_3$), 66.0 ($GeCH_2CH_2O-$), 22.0, 15.0 (aliphatic carbons) ppm. Anal. Calcd for $C_{16}H_{19}ClGeO$: C, 57.30; H, 5.71. Found: C, 57.47; H, 5.81.

Synthesis of $Et_2Ge(NMe_2)CH_2CH_2OEt$ (5a). To a solution of **4a** (2.36 g, 9.86 mmol) in benzene (35 mL) was added solid $LiNMe_2$ (0.509 g, 9.98 mmol). The resulting suspension was stirred at room temperature for 7 h and was then filtered through Celite. The volatiles were removed from the filtrate *in vacuo* to yield 2.25 g (92%) of **5a** as a clear oil. ^1H NMR (C_6D_6, 25 °C): δ 3.50 (t, J = 7.5 Hz, 2H, $GeCH_2CH_2O$), 3.29 (q, J = 7.2 Hz, 2H, q, $-OCH_2CH_3$), 2.57 (s, 6H, $-N(CH_3)_2$), 1.24 (t, J = 7.2 Hz, 3H, $-OCH_2CH_3$), 1.17−1.05 (m, 6H, $(CH_3CH_2)_2Ge$ and $GeCH_2CH_2O-$), 0.87 (t, J = 7.2 Hz, 6H, $Ge(CH_2CH_3)_2$) ppm. ^{13}C NMR (C_6D_6, 25 °C): δ 67.8 ($-OCH_2CH_3$), 65.8 ($GeCH_2CH_2O-$), 41.4 ($-N(CH_3)_2$), 15.5, 14.2, 8.8, 5.6 (aliphatic carbons) ppm. Anal. Calcd for $C_{10}H_{25}GeNO$: C, 48.44; H, 10.16. Found: C, 47.55; H, 10.51.

Synthesis of $Bu_2Ge(NMe_2)CH_2CH_2OEt$ (5b). To a solution of **4b** (1.324 g, 4.482 mmol) in benzene (35 mL) was added solid lithium dimethylamide (0.234 g, 4.59 mmol). The resulting suspension was stirred 8 h, followed by filtration through Celite to yield a clear solution. Removal of the volatiles *in vacuo* yielded **5b** (1.42 g, 92%) as a clear oil. ^1H NMR (C_6D_6, 25 °C): δ 3.54 (t, J = 7.8 Hz, 2H, $GeCH_2CH_2O$), 3.31 (q, J = 6.9 Hz, 2H, OCH_2CH_3), 2.60 (s, 6H, $N(CH_3)_2$), 1.53−1.26 (m, 10 H), 1.43 (t, J = 6.9 Hz, 3H, OCH_2CH_3), 0.92 (t, J = 6.9 Hz, 6H, $GeCH_2CH_2CH_2CH_3$), 0.89 (m, 4H, $GeCH_2CH_2CH_2CH_2CH_3$) ppm. ^{13}C NMR (C_6D_6, 25 °C): δ 68.0 ($-OCH_2CH_3$), 65.8 ($GeCH_2CH_2O-$), 41.4 ($-N(CH_3)_2$), 27.3, 26.9, 15.6, 15.0, 14.0, 13.6 (aliphatic carbons) ppm. Anal. Calcd for $C_{14}H_{33}GeNO$: C, 55.31; H, 10.94. Found: C, 54.91; H, 11.00.

Synthesis of $Ph_2Ge(NMe_2)CH_2CH_2OEt$ (5c). To a solution of **4c** (0.493 g, 1.47 mmol) in benzene (25 mL) was added solid $LiNMe_2$ (0.093 g, 1.8 mmol). The resulting suspension was stirred at room temperature for 15 h and was then filtered through Celite. The volatiles were removed from the filtrate *in vacuo* to yield 0.436 g (86%) of **5c** as a clear oil. ^1H NMR (C_6D_6, 25 °C): δ 7.70−7.67 (m, 4H, *meta*-H), 7.21−7.17 (m, 6H, *ortho*-H and *para*-H), 3.58 (t, J = 7.8 Hz, 2H, $GeCH_2CH_2O$), 3.10 (q, J = 6.9 Hz, 2H, q, $-OCH_2CH_3$), 2.78 (s, 6H, $-N(CH_3)_2$), 1.89 (t, J = 7.8 Hz, 2H, $-GeCH_2CH_2O-$), 1.00 (t, J = 6.9 Hz 3H, OCH_2CH_3) ppm. ^{13}C NMR (C_6D_6, 25 °C): δ 136.9, 134.9, 129.3, 128.3 (aromatic carbons), 67.2 ($-OCH_2CH_3$), 65.7 ($GeCH_2CH_2O-$), 41.4 ($-N(CH_3)_2$), 15.8, 15.3 (aliphatic carbons) ppm. Anal. Calcd for $C_{18}H_{25}GeNO$: C, 62.85; H, 7.32. Found: C, 63.01; H, 7.54.

Synthesis of $Ph_3GeGe(Et_2)CH_2CH_2OEt$ (6a). To a solution of **5a** (0.762 g, 3.07 mmol) in acetonitrile (15 mL) in a Schlenk tube was added Ph_3GeH (0.945 g, 3.10 mmol) in acetonitrile (10 mL). The tube was sealed with a Teflon stopper, and the reaction mixture was heated at 90 °C for 36 h. The solution was transferred to a Schlenk flask, and the volatiles were removed *in vacuo*, yielding a pale yellow oil. Kugelrohr distillation of the crude product afforded 1.179 g (75%) of **6a** as a clear oil. ^1H NMR (C_6D_6, 25 °C): δ 7.66−7.60 (m, 6H, aromatics), 7.24−7.14 (m, 9H, aromatics), 3.44 (t, J = 7.8 Hz, 2H, $GeCH_2CH_2O$), 3.14 (q, J = 6.9 Hz, 2H, $-OCH_2CH_3$), 1.49 (t, J = 6.9 Hz, 3H, $-OCH_2CH_3$), 1.17−1.01 ppm (m, 12H, $(CH_3CH_2)_2Ge$, $(CH_3CH_2)_2Ge$, and $GeCH_2CH_2O-$) ppm. ^{13}C NMR (C_6D_6, 25 °C): δ 139.2, 135.7, 128.7, 128.6 (aromatic carbons), 68.7 ($-OCH_2CH_3$), 65.7 ($GeCH_2CH_2O-$), 15.5, 15.4, 10.3, 7.2 (aliphatic carbons) ppm. Anal. Calcd for $C_{26}H_{34}Ge_2O$: C, 61.50; H, 6.75. Found: C, 61.18; H, 6.96.

Synthesis of $Ph_3Ge-Ge(Bu)_2CH_2CH_2OEt$ (6b). To a solution of **5b** (0.633 g, 2.18 mmol) in acetonitrile (15 mL) was added Ph_3GeH (0.670 g, 2.20 mmol) in acetonitrile (10 mL). The solution was refluxed for 48 h, and the volatiles were removed *in vacuo* to yield a yellow oil. The material was distilled in a Kugelrohr oven to remove the remaining Ph_3GeH, and the pot residue was isolated to yield 0.930 g (76%) of **6b** as a pale yellow oil. ^1H NMR (C_6D_6, 25 °C): δ 7.68−7.65 (m, 6H, aromatics), 7.24−7.14 (m, 9 H, aromatics), 3.51 (t, J = 7.2 Hz, 2H, $GeCH_2CH_2OEt$), 3.18 (q, J = 7.2 Hz, OCH_2CH_3), 1.56 (t, J = 7.5 Hz, 2H, $GeCH_2CH_2O$), 1.49−1.41 (m, 4H, aliphatics), 1.31−1.18 (m, 8H, aliphatics), 1.08 (t, J

= 6.9 Hz, 3H, OCH_2CH_3), 0.80 (t, J = 7.2 Hz, 6H, $-(CH_2)_3CH_3$) ppm.. ^{13}C NMR (C_6D_6, 25 °C): δ 139.1, 135.7, 128.7, 128.5 (aromatic carbons), 68.9 ($-OCH_2CH_3$), 65.6 ($GeCH_2CH_2O-$), 28.7, 26.7, 16.2, 15.4, 14.9, 13.7 (aliphatic carbons) ppm. Anal. Calcd for $C_{30}H_{42}Ge_2O$: C, 63.90; H, 7.51. Found: C, 63.55; H, 7.48.

Synthesis of $Ph_3Ge-Ge(Ph)_2CH_2CH_2OEt$ (6c). To a solution of **5c** (1.511 g, 4.392 mmol) in acetonitrile (40 mL) was added Ph_3GeH (1.339 g, 4.391 mmol) in acetonitrile (25 mL). The solution was refluxed for 48 h, and the volatiles were removed *in vacuo* to yield a yellow oil. The material was distilled in a Kugelrohr oven to remove the remaining Ph_3GeH, and the pot residue was isolated to yield 2.443 g (92%) of **6c** as a white solid. ^1H NMR (C_6D_6, 25 °C): δ 7.64−7.52 (m, 10 H, *meta*-H), 7.13−7.02 (m, 15 H, *ortho*- and *para*-H), 3.59 (t, J = 7.8 Hz, 2H, $GeCH_2CH_2O-$), 3.03 (q, J = 6.9 Hz, 2H, $-OCH_2CH_3$), 2.08 (q, J = 7.8 Hz, 2H, $GeCH_2$-CH_2O-), 0.95 (t, J = 6.9 Hz, 3H, $-OCH_2CH_3$) ppm. H, ^{13}C NMR (C_6D_6, 25 °C): δ 138.4, 138.1, 135.9, 135.5, 129.0, 128.9, 128.6, 128.5 (aromatic carbons), 68.4 ($-OCH_2CH_3$), 65.6 ($GeCH_2CH_2O-$), 17.6, 15.2 (aliphatic carbons) ppm. Anal. Calcd for $C_{34}H_{34}Ge_2O$: C, 67.63; H, 5.67. Found: C, 67.37; H, 5.44.

Synthesis of $Ph_3GeGe(Et_2)H$ (7a). To a solution of **6a** (0.600 g, 1.18 mmol) in benzene (20 mL) was added a 1.0 M solution of DIBAL-H in hexane (1.22 mL, 1.22 mmol). The solution was refluxed for 36 h, and the volatiles were removed *in vacuo* to yield a pale yellow oil. The crude material was filtered through a 1 in. × 1 in. silica gel column using 25 mL of a 9:1 benzene/acetonitrile solution as the eluent to yield 0.357 g (69%) of **7a** as a cloudy white liquid after removal of the solvent. ^1H NMR (C_6D_6, 25 °C): δ 7.67−7.61 (m, 6H, aromatics), 7.23−7.16 (m, 9H, aromatics), 4.91 (pent, J = 3.0 Hz, 1H, $Ge-H$), 1.07−1.01 (m, 10H, $Ge-(CH_2CH_3)_2$) ppm. ^{13}C NMR (C_6D_6, 25 °C): δ 139.2, 135.7, 128.7, 128.6 (aromatic carbons), 10.2, 6.2 (aliphatic carbons) ppm. IR (Nujol): 1996.1 cm^{-1} (ν_{Ge-H}). Anal. Calcd for $C_{22}H_{26}Ge_2$: C, 60.65; H, 6.01. Found: C, 60.81; H, 6.42.

Synthesis of $Ph_3Ge-Ge(Bu)_2H$ (7b). To a solution of **6b** (1.286 g, 2.280 mmol) in benzene (15 mL) was added a 1.0 M solution of diisobutylaluminum hydride (2.5 mL, 2.5 mmol) via syringe. The resulting solution was refluxed for 18 h. The volatiles were removed *in vacuo* to yield a clear viscous oil. The crude material was dissolved in hexane (5 mL) and filtered through a short column (1 in.) of silica gel using 45 mL of hexane as the eluent. The solvent was removed *in vacuo* to yield 0.585 g (52%) of **7b** as a clear oil. ^1H NMR (C_6D_6, 25 °C): δ 7.67−7.64 (m, 6H, aromatics), 7.24−7.16 (m, 9H, aromatics), 4.40 (pent, J = 3.6 Hz, 1H, Ge-H), 1.47−1.34 (m, 4H, aliphatics), 1.24 (sext, J = 7.8 Hz, 4H, $GeCH_2$-$CH_2CH_2CH_3$), 1.17−1.08 (m, 4H, aliphatics), 0.80 (t, J = 7.5 Hz, 6H, $GeCH_2CH_2CH_2CH_3$) ppm. ^{13}C NMR (C_6D_6, 25 °C): δ 139.3, 135.7, 128.7, 128.6 (aromatic carbons), 28.7, 26.7, 14.0, 13.7 (aliphatic carbons) ppm. IR (Nujol): 2036.2 cm^{-1} (ν_{Ge-H}). Anal. Calcd for $C_{26}H_{34}Ge_2$: C, 63.50; H, 6.96. Found: C, 63.60; H, 7.10.

Synthesis of $Ph_3GeGe(Et_2)Ge(Et_2)CH_2CH_2OEt$ (8a). To a solution of **7a** (0.322 g, 0.739 mmol) in acetonitrile (10 mL) was added a solution of **5a** (0.185 g, 0.746 mmol) in acetonitrile (5 mL). The reaction was sealed in a Schlenk tube and heated to 90 °C for 72 h. The volatiles were removed *in vacuo* to yield 0.425 g (90%) of **8a** as a pale yellow liquid. ^1H NMR (C_6D_6, 25 °C): δ 7.62−7.58 (m, 6H, aromatics), 7.22−7.14 (m, 9H, aromatics), 3.28 (t, J = 6.6 Hz, 2H, $GeCH_2CH_2OEt$), 3.14 (q, J = 6.9 Hz, 2H, $-OCH_2CH_3$), 1.04−0.97 (m, 17H, $Ge(CH_2CH_3)_2$ and $-OCH_2CH_3$), (0.90, t, 6H, $Ge(CH_2CH_3)_2$), 0.74 (t, 2H, J = 6.6 Hz, $GeCH_2CH_2$-OEt) ppm. ^{13}C NMR (C_6D_6, 25 °C): δ 139.2, 135.6, 128.7, 128.5 (aromatic carbons), 67.2 ($-OCH_2CH_3$), 65.9 ($GeCH_2CH_2O-$), 15.3, 14.0, 10.2, 8.6, 6.1, 5.6 (aliphatic carbons) ppm. Anal. Calcd for $C_{30}H_{44}Ge_3O$: C, 56.43; H, 6.94. Found: C, 57.23; H, 6.86.

Synthesis of $Ph_3GeGe(Bu_2)Ge(Bu_2)CH_2CH_2OEt$ (8b). To a solution of **7b** (1.777 g, 3.62 mmol) in acetonitrile (20 mL) was added a solution of **5b** (1.208 g, 3.98 mmol) in acetonitrile (10 mL). The reaction mixture was sealed in a Schlenk tube equipped with a Teflon plug and was heated at 85 °C for 48 h. The solution was transferred to a Schlenk flask, and the volatiles were removed *in vacuo*. The crude product was distilled in a Kugelrohr oven (oven temp = 100 °C, P = 0.08 Torr) for 3 h to remove excess **5b**. Yield of **8b** = 2.555 g (94%). ^1H NMR (C_6D_6, 25 °C): δ 7.73−7.65 (m, 6H, aromatics), 7.23−7.12 (m, 9 H, aromatics), 3.51 (t, J = 7.5 Hz, 2H, $GeCH_2CH_2OEt$), 3.18 (q, J = 6.9 Hz, 2H, $-OCH_2CH_3$), 1.62−1.04 (m, 24 H, aliphatics), 0.98−0.72 (m, 17 H, aliphatics) ppm. ^{13}C NMR (C_6D_6, 25 °C): δ 139.1, 135.8, 128.7, 128.5 (aromatic carbons), 68.8 ($-OCH_2CH_3$), 65.7 ($GeCH_2CH_2O-$), 31.9, 28.8, 26.8, 20.0, 16.3, 15.0, 14.0, 13.8, 10.4, 7.1 (aliphatic carbons) ppm. Anal. Calcd for $C_{38}H_{60}Ge_4O$: C, 60.79; H, 8.05. Found: C, 60.43; H, 8.39.

Synthesis of $Ph_3GeGe(Et_2)Ge(Et_2)H$ (9a). A solution of **8a** (0.217 g, 0.340 mmol) in benzene (15 mL) was treated with a 1.0 M hexane solution of DIBAL-H (0.35 mL, 0.35 mmol), and the mixture was refluxed under N_2 for 18 h. The volatiles were removed *in vacuo* to yield a clear oil, which was washed on a silica column (1 in. h × 1 in. dia) using benzene as the eluent (30 mL). The benzene was removed *in vacuo*, and the resulting oil was distilled using a Kugelrohr oven (oven temp = 115 °C, P = 0.07 Torr) to remove any remaining impurities for 3 h to yield **9a** as a clear oil (0.079 g, 41%). ^1H NMR (C_6D_6, 25 °C): δ 7.64−7.61 (m, 6H, aromatics), 7.22−7.17 (m, 9H, aromatics), 4.31 (pent, J = 3.2 Hz, 1 H, Ge-H), 1.03 (m, 20 H, aliphatics) ppm. (^{13}C NMR?) IR (Nujol): 1996.4 cm^{-1} (ν_{Ge-H}). We were not able to obtain a satisfactory elemental analysis for **9a**.

Synthesis of $Ph_3GeGe(Bu_2)Ge(Bu_2)H$ (9b). A solution of **8b** (1.965 g, 2.61 mmol) in benzene (40 mL) was treated with a 1.0 M hexane solution of DIBAL-H (2.88 mL), and the mixture was refluxed under N_2 for 48 h. The volatiles were removed *in vacuo* to yield a clear oil, which was washed on a silica column (1 in. h × 1 in. dia) using benzene as the eluent (45 mL). The benzene was removed *in vacuo*, and the resulting oil was distilled using a Kügelrohr oven (oven temp = 110 °C, P = 0.05 Torr) for 5 h to remove impurities to yield **9b** as a clear oil (0.580 g, 33%). ^1H NMR (C_6D_6, 25 °C): δ 7.74−7.63 (m, 6H, aromatics), 7.23−7.12 (m, 9H, aromatics), 4.91 (pent, J = 3.0 Hz, 1H, Ge-H), 1.61−1.09 (m, 24H, aliphatics), 0.80 (t, J = 7.2 Hz, 12H, $-CH_2CH_2CH_2CH_3$) ppm. ^{13}C NMR (C_6D_6, 25 °C): δ 139.2, 135.7, 128.7, 128.5 (aromatic carbons), 30.6, 28.7, 26.7, 26.2, 14.0, 13.7, 10.3, 7.05 (aliphatic carbons) ppm. IR (Nujol): 2000.0 cm^{-1} (ν_{Ge-H}). We were not able to obtain a satisfactory elemental analysis for **9b**.

Synthesis of $Ph_3GeGe(Et_2)Ge(Et_2)Ge(Et_2)CH_2CH_2OEt$ (10a). To a solution of **9a** (0.056 g, 0.099 mmol) in acetonitrile (10 mL) was added a solution of **5a** (0.025 g, 0.104 mmol) in acetonitrile (10 mL). The reaction mixture was sealed in a Schlenk tube equipped with a Teflon plug, and the reaction mixture was heated at 85 °C for 48 h. The solution was transferred to a Schlenk flask, and the volatiles were removed *in vacuo*. The crude product was distilled in a Kugelrohr oven (oven temp = 115 °C, P = 0.07 Torr) to remove excess **5a**, yielding **10a** (0.073 g, 97%) as a viscous clear oil. ^1H NMR (C_6D_6, 25 °C): δ 7.62−7.59 (m, 6H, aromatics), 7.25−7.12 (m, 9H, aromatics), 3.59 (t, J = 7.5 Hz, 2H, $GeCH_2CH_2$-OEt), 3.30 (q, J = 6.8 Hz, 2H, $-OCH_2CH_3$), 1.36 (t, J = 7.8 Hz, 3H $-OCH_2CH_3$), 1.18−0.89 (m, 32 H, aliphatics) ppm. ^{13}C NMR (C_6D_6, 25 °C): δ 139.2, 135.6, 128.7, 128.6, 67.5 ($-OCH_2CH_3$), 65.8 ($GeCH_2CH_2O-$), 19.1, 15.5, 14.0, 10.5, 10.2, 8.6, 8.3, 6.1 (aliphatic carbons) ppm. UV/visible: λ_{max} 241 ($\epsilon = 1.8 \times 10^4$ L mol^{-1} cm^{-1}). Anal. Calcd for $C_{34}H_{54}Ge_4O$: C, 53.09; H, 7.08. Found: C, 53.29; H, 7.22.

Synthesis of $Ph_3GeGe(Bu_2)Ge(Bu_2)Ge(Bu_2)CH_2CH_2OEt$ (10b). To a solution of **9b** (0.370 g, 0.540 mmol) in acetonitrile (10 mL) was added a solution of **5b** (0.174 g, 0.570 mmol) in acetonitrile (10 mL). The reaction mixture was sealed in a Schlenk tube equipped with a Teflon plug, and the reaction mixture was heated at 85 °C for 48 h. The solution was transferred to a Schlenk flask, and the volatiles were removed *in vacuo*. The crude product was distilled in a Kugelrohr oven (oven temp = 105 °C, $P = 0.03$ Torr) to remove excess **5b**, yielding **10b** (0.430 g, 85%) as a viscous clear oil. ^{1}H NMR (C_6D_6, 25 °C): δ 7.70−7.58 (m, 6H, aromatics), 7.23−7.08 (m, 9H, aromatics), 3.35 (t, $J = 7.2$ Hz, 2H, $GeCH_2CH_2$-OEt), 3.19 (q, $J = 6.0$ Hz, 2H, $-OCH_2CH_3$), 1.52−1.02 (m, 29H, aliphatics), 0.94−0.72 (m, 30H, aliphatics) ppm. ^{13}C NMR (C_6D_6, 25 °C): δ 139.2, 135.6, 128.7, 128.5, 68.5 ($-OCH_2CH_3$), 65.8 ($GeCH_2CH_2O-$), 31.9, 28.7, 28.6, 26.7, 22.9, 16.2, 15.4, 15.0, 14.4, 14.2, 14.0, 13.7, 10.3, 7.0 (aliphatic carbons) ppm. UV/visible: λ_{max} 235 ($\epsilon = 1.4 \times 10^4$ L mol^{-1} cm^{-1}). Anal. Calcd for $C_{46}H_{78}Ge_4O$: C, 58.93; H, 8.38. Found: C, 58.85; H, 8.11.

Preparation of 10b Directly from 8b. To a solution of **8b** (0.94 g, 1.14 mmol) in benzene (30 mL) in a Schlenk flask was added a 1 M solution of DIBAL-H in hexane (1.50 mL, 1.50 mmol). The resulting solution was refluxed under N_2 for 24 h and allowed to cool, and the volatiles were removed *in vacuo*, yielding a pale yellow oil. The product was directly transferred to a Schlenk tube, where a solution of **5b** (0.380 g, 1.25 mmol) in acetonitrile (30 mL) was added. The tube was sealed with a Teflon plug and heated at 95 °C for 48 h. The volatiles were removed *in vacuo*, resulting in an orange oil. The crude material was filtered through a 1 in. × 1 in. silica gel column using 40 mL of benzene as the eluent to yield 0.876 g (75%) of **10b** as a pale yellow liquid after removal of the solvent. The identity of **10b** was confirmed by NMR (^{1}H and ^{13}C) spectroscopy.

Synthesis of Bu_3GeCH_2CN. To a solution of $HN(Pr^i)_2$ (0.70 mL, 5.0 mmol) in THF (20 mL) was added a 2.5 M solution of Bu^nLi in hexane (2.04 mL, 5.1 mmol) at −78 °C. The solution was stirred for 30 min, and acetonitrile (0.27 mL, 5.2 mmol) was added. The resulting suspension was placed in a −30 °C bath, and a solution of Bu_3GeCl (1.391 g, 4.97 mmol) in THF (15 mL) was added at this temperature. The reaction mixture was allowed to come to room temperature and was stirred for 12 h. The volatiles were removed *in vacuo* to yield a white solid, which was dissolved in hexane (15 mL) and filtered through Celite. Removal of the volatiles yielded Bu_3GeCH_2CN, 1.19 g (84%). ^{1}H NMR (C_6D_6, 25 °C): δ 1.82−1.49 (m, 20H, $Ge(CH_2CH_2CH_2CH_3)_3$ and $GeCH_2$-CN), 1.08 (t, $J = 7.2$ Hz, 9H, $Ge(CH_2CH_2CH_2CH_3)_3$ ppm. ^{13}C NMR (C_6D_6, 25 °C): δ 68.1 ($-CH_2CN$), 28.4, 27.5, 25.7 (butyl group carbons), 16.0 ($GeCH_2CN$), 14.3 ($-CH_2CH_2CH_2CH_3$) ppm.

Synthesis of 1 Using Bu_3GeCH_2CN. A Schlenk tube was charged with Bu_3GeCH_2CN (0.253 g, 0.890 mmol) in acetonitrile (10 mL). To this was added a solution of Ph_3GeH (0.270 g, 0.885 mmol) in acetonitrile (10 mL). The tube was sealed with a Teflon plug and was heated at 90 °C for 50 min, and the solution was transferred to a Schlenk flask. The volatiles were removed *in vacuo*, yielding 0.434 g (89%) of **1**. The identity of **1** was confirmed by NMR (^{1}H and ^{13}C) spectroscopy.

Table 3. Crystallographic Data for Compounds 1 and 2

	1	**2**
formula	$C_{30}H_{42}Ge_2$	$C_{24}H_{27}Ge_2$
space group	$P\bar{1}$	$R\bar{3}$
a (Å)	10.051(3)	15.533(1)
b (Å)	15.141(4)	15.533(1)
c (Å)	20.970(6)	16.275(3)
α (deg)	109.043(4)	90
B (deg)	100.239(4)	90
γ (deg)	98.645(4)	120
V (Å^3)	2893.1(1)	3400.4(7)
Z, Z′	4, 2	6, 1
ρ_{calc} (g cm^{-3})	1.258	1.350
temperature (K)	215(2)	213(2)
radiation	Mo Kα	Mo Kα
wavelength (Å)	0.71073	0.71073
R	0.0485	0.0333
R_w	0.1199	0.0932

X-ray Structure Determination. Diffraction intensity data were collected with a Siemens P4/CCD diffractometer. Crystallographic data and details of X-ray studies are shown in Table 3. The asymmetric unit of **1** contains two crystallographically independent but chemically equivalent molecules. 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 SHEXTL (5.10) program package (G. Sheldrick, Bruker XRD, Madison, WI). ORTEP diagrams were drawn using the ORTEP3 program (L. J. Farrugia, Glasgow).

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Supporting Information Available: Crystallographic data for **1** and **2** in cif format. This information is available free of charge via the Internet at http://pubs.acs.org.

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