Articles

Preparation, Structure, and Reactivity of Discrete Branched Oligogermanes[⊥]

Monika L. Amadoruge,[†] James A. Golen,[‡] Arnold L. Rheingold,[§] and Charles S. Weinert*[,†]

Department of Chemistry, Oklahoma State University, Stillwater, Oklahoma 74078, Department of Chemistry and Biochemistry, University of Massachusetts Dartmouth, 285 Old Westport Road, North Dartmouth, Massachusetts 02747-2300, and Department of Chemistry and Biochemistry, University of California—San Diego, 9500 Gilman Drive MC 0332, La Jolla, California 92093

Received September 15, 2007

The hydrogermolysis reaction of $PhGeH_3$ serves in the synthesis of discrete branched oligogermanes. Treatment of $PhGeH_3$ with 3 equiv of the α-germyl nitriles R_3GeCH_2CN ($R_3 = Ph_3$ or $Bu_2CH_2CH_2OEt$), which are generated in situ from the corresponding amides R_3GeNMe_2 and CH_3CN, furnishes the tetragermanes $PhGe(GePh_3)_3$ and $PhGe(GeBu_2CH_2CH_2OEt)_3$ in excellent yield. The crystal structure of $PhGe(GePh_3)_3$ was determined. This compound is the first branched oligogermane to be structurally characterized. Reaction of the tetragermane $PhGe(GeBu_2CH_2CH_2OEt)_3$ with $Bu^i{}_2AlH$ generated the intermediate hydride $PhGe(GeBu_2H)_3$. Subsequent treatment of $PhGe(GeBu_2H)_3$ with the synthons $R_2Ge(NMe_2)CH_2CH_2OEt$ (R = Bu, Et, Ph) in CH_3CN solution furnished the heptagermanes $PhGe(GeBu_2GeR_2CH_2CH_2OEt)_3$ (R = Bu, Et, Ph). The latter process also proceeds through the in situ formation of the α-germyl nitriles $R_2Ge(CH_2CN)CH_2CH_2OEt$.

Introduction

Catenated compounds of the heavier group 14 elements are of significant interest. Although they structurally resemble saturated hydrocarbons, their physical properties more closely resemble those of conjugated unsaturated hydrocarbons. This phenomenon results from the inherent σ-delocalization along the element—element backbone present in these molecules that imparts intriguing electronic and optical properties.[1–14] In the case of oligomeric germanium compounds containing germanium–germanium single bonds and organic side groups, the position of the absorption maximum (λ_{max}) undergoes a bathochromic shift[9,15] and the oxidation potential[16,17] and ionization potential[10] of the individual molecules decreases as the length of the Ge–Ge chain increases. Similar effects have also been observed in related tin-containing systems.[7,8,18]

Branched group 14 catenates can be regarded as a two-dimensional array of elements where the presence of branching results in an overall increase in the σ-delocalization in these molecules versus related linear systems.[19] This is attributed to the interaction of the individual arms of the branched system and is manifested in a red shift and broadening of the λ_{max} peak versus those observed for linear polymers.[20,21] Branched group 14 oligomers are rare and for the tin-containing species only a few examples have been reported. These include $RSn(SnMe_3)_3$ (R = Me, Et, Bu^n, Bu^i, $C_5H_{11}{}^n$, or Ph),[22] as well as the lithium salt $LiSn(SnMe_3)_3$[23] and the neopentane analogues $Sn(SnR_3)_4$

---

[*] Author to whom correspondence should be addressed. E-mail: weinert@chem.okstate.edu.

[⊥] Dedicated to Dr. Arthur J. Ashe, III, upon his retirement from the faculty at the University of Michigan.

[†] Oklahoma State University.

[‡] University of Massachusetts Dartmouth.

[§] University of California-San Diego.

(1) Ortiz, J. V. *Polyhedron* **1991**, *10*, 1285–1297.

(2) Miller, R. D.; Michl, J. *Chem. Rev.* **1989**, *89*, 1359–1410.

(3) Balaji, V.; Michl, J. *Polyhedron* **1991**, *10*, 1265–1284.

(4) Rivière, P.; Rivière-Baudet, M.; Satgé, J. In *Comprehensive Organometallic Chemistry*; Abel, E. W., Ed.; Pergamon: New York, 1982; Vol. 2, pp 399–518..

(5) Rivière, P.; Rivière-Baudet, M.; Satgé, J. In *Comprehensive Organometallic Chemistry II*; Wilkinson, G., Ed.; Pergamon: New York, 1995; Vol. 2, pp 137–216..

(6) Weinert, C. S. In *Comprehensive Organometallic Chemistry III*; Crabtree, R. H., Mingos, D. M. P., Eds.; Elsevier: Oxford, UK, 2007; Vol. *3*, pp699–808..

(7) Sita, L. R. *Acc. Chem. Res.* **1994**, *27*, 191–197.

(8) Sita, L. R. *Adv. Organomet. Chem.* **1995**, *38*, 189–243.

(9) Mochida, K.; Chiba, H. *J. Organomet. Chem.* **1994**, *473*, 45–54.

(10) Mochida, K.; Hata, R.; Shimoda, M.; Matsumoto, F.; Kurosu, H.; Kojima, A.; Yoshikawa, M.; Masuda, S.; Harada, Y. *Polyhedron* **1996**, *15*, 3027–3032.

(11) Dräger, M.; Ross, L.; Simon, D. *Rev. Silicon, Germanium, Tin, Lead Compds.* **1983**, *7*, 299–445.

(12) Abd-El-Aziz, A. S.; Carraher, C. E., Jr.; Pittman, C. U., Jr.; Sheats, J. E.; Zeldin, M. *Macromolecules Containing Metal and Metal-Like Elements*; Wiley Interscience: Hoboken, NJ, 2003; Vol. 1.

(13) Glockling, F. *The Chemistry of Germanium*; Academic Press: London, UK, 1969.

(14) Lesbre, M.; Mazerolles, P.; Satgé, J. *The Organic Compounds of Germanium*; Wiley Interscience: London, UK, 1971.

(15) Bulten, E. J.; Noltes, J. G. *J. Organomet. Chem.* **1969**, *16*, P8–P10.

(16) Okano, M.; Mochida, K. *Chem. Lett.* **1990**, 701–704.

(17) Mochida, K.; Hodota, C.; Hata, R.; Fukuzumi, S. *Organometallics* **1993**, *12*, 586–588.

(18) Sita, L. R. *Organometallics* **1992**, *11*, 1442.

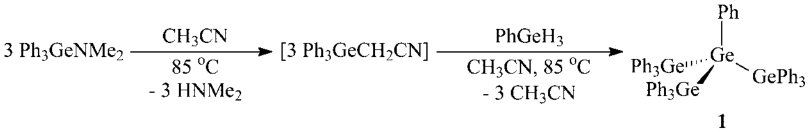
(19) Watanabe, A. *J. Organomet. Chem.* **2003**, *685*, 122–133.

(20) Watanabe, A.; Miike, H.; Tsutsumi, Y.; Matsuda, M. *Macromolecules* **1993**, *26*, 2111–2116.

(21) Hatanaka, Y.; Okada, S.; Onozawa, S.; Suzuki, Y.; Tanaka, M. *Chem. Lett.* **2001**, 600–601.

10.1021/om800040f CCC: $40.75

Scheme 1



1
85 %

($R = Me$[22] or Ph[24]). A series of longer chain branched perbutyl polystannanes has also been reported.[25]

In the case of germanium, the synthesis of only two examples of shorter chain species has been described. The hydride $HGe(GePh_3)_3$ was obtained by the reaction of Ph_3GeLi with GeI_2. Subsequent treatment of the hydride with Bu^nLi followed by the addition of MeI furnished the methyl derivative $MeGe(GePh_3)_3$.[26] In addition, ^{13}C NMR data in $CDCl_3$ for the branched oligomers $PhGe(GePh_3)_3$ and $Ge(GePh_3)_4$ have been reported,[27] but no details describing their syntheses were given.

We have employed the hydrogermolysis reaction for the preparation of two different series of linear oligogermanes[28] as well as several digermanes.[28,29] The starting reagents used were a germanium hydride R_3GeH and a germanium amide R_3GeNMe_2. The use of CH_3CN as the solvent is crucial for the success of this reaction, and we have demonstrated[28,29] that the actual germanium−germanium bond-forming process occurs via an α-germyl nitrile R_3GeCH_2CN intermediate formed in the reaction of the amide with the CH_3CN solvent. The R_3GeCH_2CN intermediate contains a labile Ge–C bond[30,31] that undergoes reaction with germanium hydrides. Thus, CH_3CN serves both as a reagent and the solvent in this reaction.

We report here the preparation of branched oligogermanes using the hydrogermolysis reaction. This method has been employed for the synthesis of $PhGe(GePh_3)_3$ for which the X-ray structure was obtained, representing the first structurally characterized branched oligogermane. In addition, we also prepared and characterized the functionally substituted branched tetragermane $PhGe(GeBu_2CH_2CH_2OEt)_3$, which was subsequently employed for the synthesis of the heptagermanes $PhGe(GeBu_2GeR_2CH_2CH_2OEt)_3$ ($R = Bu$, Et, Ph).

Results and Discussion

The branched tetragermane $PhGe(GePh_3)_3$ (**1**) was prepared by reaction of $PhGeH_3$ with 3 equiv of Ph_3GeNMe_2 in CH_3CN solution, which proceeds though the formation of the intermediate α-germyl nitrile Ph_3GeCH_2CN as shown in Scheme 1. The ^1H NMR spectrum of **1** in C_6D_6 contains two distinct doublets at δ 7.66 ($J = 7.5$ Hz) and 7.26 ($J = 7.5$ Hz) ppm in an integrated ratio of 1:9 due to the ortho-protons of the mono- and triphenylgermyl groups, respectively. The ^{13}C NMR spectrum of **1** in C_6D_6 exhibits the expected eight lines with resonances for the two different types of *ipso*-carbon atoms of the phenyl groups appearing at δ 138.9 and 138.6 ppm. The upfield peak corresponds to the *ipso*-carbon of the monophenyl germyl group since its attachment to the three $–GePh_3$ groups would be expected to have a slight shielding effect. These ^{13}C NMR chemical shift values are similar to those which were reported for **1** in $CDCl_3$ solvent.[27]

Table 1. Selected bond distances (Å) and angles (deg) for $PhGe(GePh_3)_3 \cdot C_7H_8$ (1)$\cdot C_7H_8$

Ge(1)–Ge(2)	2.4552(4)	Ge(2)–Ge(1)–Ge(3)	107.41(1)
Ge(1)–Ge(3)	2.4753(4)	Ge(2)–Ge(1)–Ge(4)	115.70(1)
Ge(1)–Ge(4)	2.4772(4)	Ge(3)–Ge(1)–Ge(4)	115.06(1)
Ge(1)–C(1)	1.971(2)	C(1)–Ge(1)–Ge(2)	107.51(7)
Ge(2)–C(7)	1.961(2)	C(1)–Ge(1)–Ge(3)	103.07(7)
Ge(2)–C(13)	1.954(2)	C(1)–Ge(1)–Ge(4)	107.12(7)
Ge(2)–C(19)	1.961(2)	C(7)–Ge(2)–C(13)	109.0(1)
Ge(3)–C(25)	1.959(3)	C(7)–Ge(2)–C(19)	103.9(1)
Ge(3)–C(31)	1.959(2)	C(13)–Ge(2)–C(19)	108.7(1)
Ge(3)–C(37)	1.959(2)	C(7)–Ge(2)–Ge(1)	116.6(8)
Ge(4)–C(43)	1.962(2)	C(13)–Ge(2)–Ge(1)	109.3(7)
Ge(4)–C(49)	1.963(3)	C(19)–Ge(2)–Ge(1)	109.0(7)
Ge(4)–C(55)	1.965(2)	C(25)–Ge(3)–C(31)	107.7(1)
		C(25)–Ge(3)–C(37)	106.4(1)
		C(31)–Ge(3)–C(37)	108.0(1)
		C(25)–Ge(3)–Ge(1)	113.90(7)
		C(31)–Ge(3)–Ge(1)	106.29(7)
		C(37)–Ge(3)–Ge(1)	114.26(7)
		C(43)–Ge(4)–C(49)	109.8(1)
		C(43)–Ge(4)–C(55)	106.8(1)
		C(49)–Ge(4)–C(55)	106.7(1)
		C(43)–Ge(4)–Ge(1)	108.51(7)
		C(49)–Ge(4)–Ge(1)	112.28(7)
		C(55)–Ge(4)–Ge(1)	112.63(7)

The X-ray crystal structure of **1** was determined and an ORTEP diagram is shown in Figure 1 while selected bond distances and angles are collected in Table 1. Compound **1**

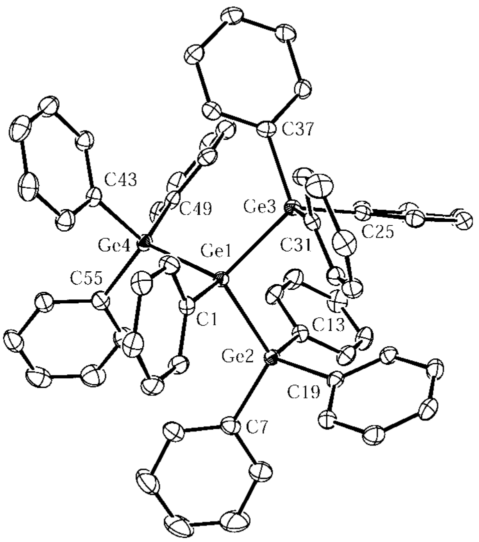


Figure 1. ORTEP diagram of $PhGe(GePh_3)_3 \cdot C_7H_8$ ($\mathbf{1} \cdot C_7H_8$). Thermal ellipsoids are drawn at 50% probability. The molecule of toluene is not shown.

---

(22) Mitchell, T. N.; El-Behairy, M. *J. Organomet. Chem.* **1977**, *141*, 43–48.

(23) Kobayashi, K.; Kawanisi, M.; Hitomi, T.; Kozima, S. *J. Organomet. Chem.* **1982**, *233*, 299–311.

(24) Willemsens, L. C.; van der Kerk, G. J. M. *J. Organomet. Chem.* **1964**, *2*, 260–264.

(25) Babcock, J. R.; Sita, L. R. *J. Am. Chem. Soc.* **1996**, *118*, 12481–12482.

(26) Glockling, F.; Hooton, K. A. *J. Chem. Soc. A* **1963**, 1849–1854.

(27) Häberle, K.; Dräger, M. *Z. Anorg. Allg. Chem.* **1987**, *551*, 116–122.

(28) Subashi, E.; Rheingold, A. L.; Weinert, C. S. *Organometallics* **2006**, *25*, 3211–3219.

(29) Amadoruge, M. L.; DiPasquale, A. G.; Rheingold, A. L.; Weinert, C. S. *J. Organomet. Chem.*, in press (DOI: 10.1016/j.organchem.2008.01.045).

(30) Rivière-Baudet, M.; Rivière, P. *J. Organomet. Chem.* **1976**, *116*, C49–C52.

(31) Rivière-Baudet, M. *Main Group Met. Chem.* **1995**, *18*, 353–385.

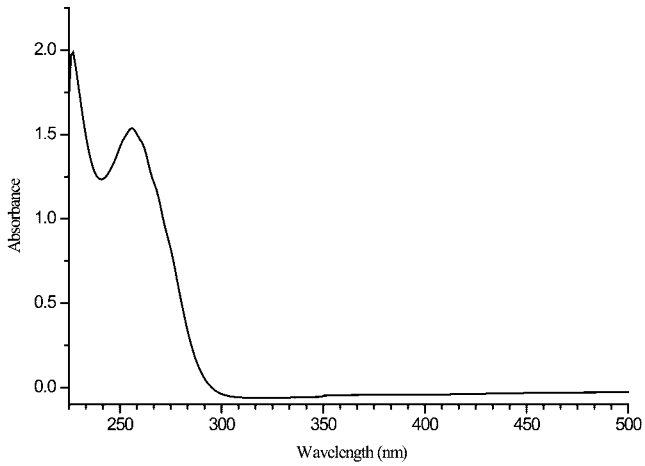


Figure 2. UV/visible spectrum of $PhGe(GePh_3)_3$ (**1**) in hexane.

contains a significantly distorted tetrahedral environment at Ge(1) with an average Ge–Ge–Ge bond angle of 112.72(1)°. The Ge(2)–Ge(1)–Ge(3) angle is more acute than the other two Ge–Ge–Ge bond angles at Ge(1) by approximately 8°, which is due to the steric repulsion of the phenyl groups bound to Ge(4) with those attached to Ge(2) and Ge(3). The average C–Ge(1)–Ge angle is acute (105.90(7)°) and two of these bond angles are more obtuse than the remaining one. The geometries at each of the three germanium atoms of the $–GePh_3$ groups are very similar and each Ge atom is also in a distorted tetrahedral environment, although the degree of distortion is less in these three cases than that observed at Ge(1). The average C–Ge–C and C–Ge–Ge angles among Ge(2), Ge(3), and Ge(4) fall into the narrow ranges of 107.2(1)–107.8° and 111.4(1)–111.6(1)°, respectively.

The average Ge–Ge distance in **1** is 2.469(4) Å, which is elongated relative to both linear and cyclic oligogermanes bearing similar organic substituents. The series of digermanes $R_3GeGePh_3$ (R = Me,[32] Et,[28] Pr^i,[29] Bu^n,[28] Ph[33]) have average Ge–Ge distances in the range 2.418(1)–2.4637(7) Å while the series of higher linear oligomers Ge_nPh_{2n+2} have average Ge–Ge bond lengths of 2.440(2) ($n = 3$),[34] 2.460(3) ($n = 4$),[34] and 2.460(4) Å ($n = 5$).[35] The average Ge–Ge distances in the series of cyclic oligomers Ge_nPh_{2n} (n = 4–6) are slightly longer, ranging from 2.457(2) to 2.465(2) Å.[36–38] The elongated Ge–Ge distances in **1** are a manifestation of the steric crowding present about the Ge_4 skeleton. The Ge–C distances to the *ipso*-carbon atoms of the phenyl substituents in **1** are typical and range from 1.954(2) to 1.971(2) Å, where the longest Ge–C bond is that of the monophenyl germanium group, which is likely elongated due to an electronic effect resulting from the attachment of Ge(1) to three other germanium atoms.

The UV/visible spectrum of **1**, shown in Figure 2, exhibits a clearly defined absorption maximum at 256 nm resulting from the $\sigma \rightarrow \sigma^*$ transition. The presence of branching in oligomeric and polymeric group 14 compounds has been shown experimentally and theoretically to result in a red shift of the λ_{max} due to an enhancement of the σ-delocalization present in these systems versus their linear analogues.[19–21,39] The absorbance maximum of **1** can be compared to those for the $\sigma \rightarrow \sigma^*$ transitions in Ge_3Ph_8 and Ge_4Ph_{10} observed at 249 and 282 nm, respectively.[34] The position of the λ_{max} for **1** is very similar to that of the trigermane rather than the tetragermane, which is as expected since the structure of **1** can be regarded as one having three overlapping Ge_3 chains, and the red shift of the λ_{max} for **1** versus that of Ge_3Ph_8 can be attributed to its branched structure.

The longer Ge–C distance of the monophenyl germanium group in **1** suggests that this bond might be weaker than the other nine $Ge-C_{ipso}$ bonds. Triflic acid has been shown to selectively cleave an aromatic Ge–C bond in the presence of aliphatic Ge–C bonds. The selectivity of this reaction in the presence of different aryl groups has also been described.[40,41] Studies conducted on a small scale and a larger preparative scale indicated that reaction of **1** with exactly 1 equiv of triflic acid furnished a monotriflate compound presumed to be $(F_3CO_2SO)Ge(GePh_3)_3$ (**2**) that exhibited a single resonance at δ −77.7 ppm in its ^{19}F NMR spectrum (Scheme 2). The free triflate anion has C_{3v} symmetry and coordination to a metal center reduces the symmetry to C_s, resulting in the expected appearance of two bands for the degenerate $\upsilon_{as}(SO_3)$ stretching mode as opposed to one feature in the free ion. The IR spectrum of **2** in a Nujol mull exhibited bands at 1305 and 1261 cm^{-1} corresponding to the $\upsilon_{as}(SO_3)$ modes. Sharp features at 1200 and 1150 cm^{-1} for the $\upsilon_s(CF_3)$ and $\upsilon_{as}(CF_3)$ modes, respectively, and a band at 937 cm^{-1} due to the $\upsilon_s(SO_3)$ stretching mode were also observed, where assignments for these bands are based on those for $Ph_3GeOSO_2CF_3$,[42] $AgOSO_2CF_3$,[43] $NaOSO_2CF_3$,[44] and the normal coordinate analysis conducted for $[Bu_4N][OSO_2CF_3]$.[45]

Subsequent treatment of **2** with an ethereal solution of $LiAlH_4$ generated the hydride $HGe(GePh_3)_3$ (**3**) as shown by ^1H NMR and IR spectroscopy and elemental analysis. The ^1H NMR spectrum of **3** contains a single hydride resonance at δ 5.85 ppm and a doublet for the *o*-hydrogen atoms of the $–GePh_3$ groups is clearly visible at 7.26 (J = 8.1 Hz) ppm. The IR spectrum of **3** contains a Ge–H stretching band at υ 1953 cm^{-1} and this feature is identical with the value reported in the literature for $(Ph_3Ge)_3GeH$.[26]

We have previously described the stepwise synthesis of linear oligogermanes which was achieved by attachment of a β-ethoxyethyl side group at the terminus of the Ge–Ge chain.[28] Cleavage of this moiety with diisobutylaluminum hydride (DIBAL-H) followed by treatment of the resulting hydride with a germanium amide in CH_3CN solution resulted in the incorporation of an additional germanium atom into the backbone.[28] This methodology is also applicable for the stepwise synthesis of branched oligomers. The branched tetragermane $PhGe(GeBu_2CH_2CH_2OEt)_3$ (**4**) was prepared in 95% yield starting with $PhGeH_3$ and the amide $Bu_2Ge(NMe_2)CH_2CH_2OEt$ (**5a**) in CH_3CN as shown in Scheme 3. The formation of the Ge–Ge bond in **4** again proceeded via initial conversion of **5a**

---

(32) Párkányi, L.; Kálmán, A.; Sharma, S.; Nolen, D. M.; Pannell, K. H. *Inorg. Chem.* **1994**, *33*, 180–182.

(33) Dräger, M.; Ross, L. *Z. Anorg. Allg. Chem.* **1980**, *469*, 115–122.

(34) Roller, S.; Simon, D.; Dräger, M. *J. Organomet. Chem.* **1986**, *301*, 27–40.

(35) Roller, S.; Dräger, M. *J. Organomet. Chem.* **1986**, *316*, 57–65.

(36) Ross, L.; Dräger, M. *J. Organomet. Chem.* **1980**, *199*, 195–204.

(37) Ross, L.; Dräger, M. *Z. Anorg. Allg. Chem.* **1984**, *519*, 225–232.

(38) Dräger, M.; Ross, L. *Z. Anorg. Allg. Chem.* **1981**, *476*, 95–104.

(39) Seki, S.; Acharya, A.; Koizumi, Y.; Saeki, A.; Tagawa, S.; Mochida, K. *Chem. Lett.* **2005**, *34*, 1690–1691.

(40) Uhlig, W. *J. Organomet. Chem.* **1991**, *409*, 377–383.

(41) Katz, S. M.; Reichl, J. A.; Berry, D. H. *J. Am. Chem. Soc.* **1998**, *120*, 9844–9849.

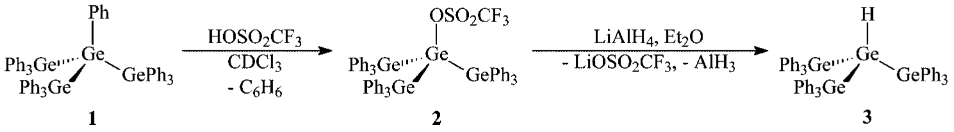
(42) Angus-Dunne, S. J.; Chin, L. E. P. L.; Burns, R. C.; Lawrance, G. A. *Trans. Met. Chem.* **2006**, *31*, 268–275.

(43) Bürger, H.; Burczyk, K.; Blaschette, A. *Monatsh. Chem.* **1970**, *101*, 102–119.

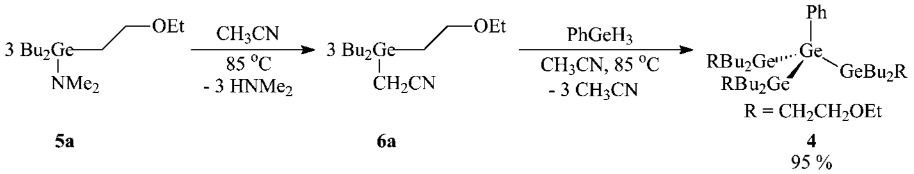
(44) Miles, M. G.; Doyle, G.; Cooney, R. P.; Tobias, R. S. *Spectrochim. Acta A* **1969**, *25*, 1515–1526.

(45) Johnston, D. H.; Shriver, D. F. *Inorg. Chem.* **1993**, *32*, 1045–1047.

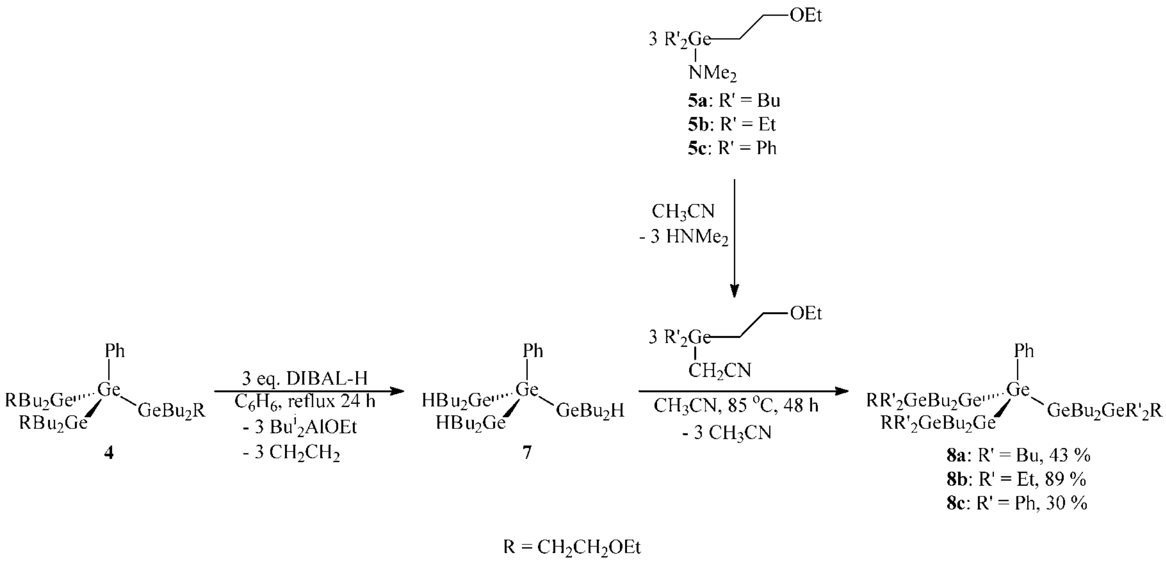
Scheme 2



Scheme 3



Scheme 4



to the α-germyl nitrile **6a** upon reaction of the amide with CH_3CN, which then underwent reaction with $PhGeH_3$ to furnish the product. The ^1H NMR spectrum of **4** exhibits resonances at δ 3.59 and 3.31 ppm for the protons of the methylene groups adjacent to the oxygen atom and the UV/visible spectrum of **4** exhibits a broad absorption maximum centered at 234 nm (Figure 3). This feature appears at higher energy than that observed for compound **1**, which is likely due to the presence of the electron-withdrawing phenyl groups bound to the germanium atoms in **1** versus the inductively electron-donating alkyl (butyl and ethoxyethyl) groups in **4**, resulting in a larger $\sigma \rightarrow \sigma^*$ gap in **4** versus that for compound **1**.

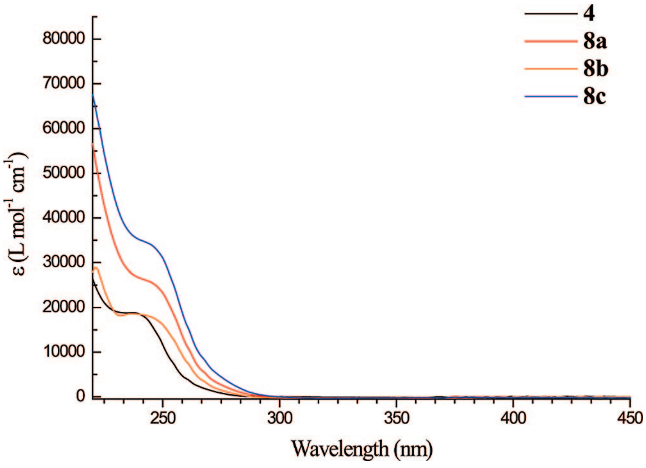


Figure 3. Overlaid UV/visible spectra (in hexane) of $PhGe(GeBu_2CH_2CH_2OEt)_3$ (**4**) and $PhGe(GeBu_2GeR_2CH_2CH_2OEt)_3$ (**8a**: R = Bu; **8b**: R = Et; **8c**: R = Ph).

Reaction of **4** with 3 equiv of DIBAL-H furnishes the intermediate hydride **7**, which was not isolated but rather was dissolved in CH_3CN and treated with 3 equiv of **5a**−**c** to generate the branched heptagermanes **8a**−**c** in moderate to good yields after purification (Scheme 4). The ^1H spectra of **8a** and **8b** exhibit resonances for the methylene groups adjacent to the oxygen atoms which are shifted from those of **4**, appearing at δ 3.67 and 3.41 ppm (**8a**) and δ 3.36 and 3.23 ppm (**8b**). The resonances for these methylene groups in the phenyl derivative **8c** are similar to those of **4** appearing at δ 3.59 and 3.32 ppm. The absorption maxima of **8a**−**c** are shown in Figure 3 and are all slightly red-shifted relative to that of **4**, having λ_{max} values of 240 (**8a**), 236 (**8b**), and 242 (**8c**) nm. The extension of each of the three arms of the oligomer by one germanium atom thus appears to have a small but measurable effect on the energy difference between the σ and σ^* orbitals in these molecules. The λ_{max} values of **4** and **8a**−**c** are all broadened and red-shifted relative to that of the linear tetragermane $Ph_3Ge[Ge(Et_2)]_3CH_2CH_2OEt$, which was observed at 235 nm.[28] However, these values are similar in energy to that of the butylated derivative $Ph_3Ge(GeBu_2)_3CH_2CH_2OEt$ (241 nm).[28] The combination of inductive effects from the attached organic groups in the linear oligomers and branching present in compounds **4**

---

(46) Shriver, D. F.; Drezdzon, M. A. *The Manipulation of Air Sensitive Comounds*, 2nd ed.; John Wiley and Sons: New York, 1986.

and **8a**−**c** therefore appear to have varying contributions to the overall relative energies of the σ and σ^* orbitals in these systems. The preparation of **8a–c** from compound **4** suggests that these compounds and related derivatives can thus serve as useful building blocks for the rational construction of higher branched oligomers and also possibly dendridic structures.

Experimental Section

All manipulations were carried out under an inert N_2 atmosphere with standard Schlenk, syringe, and glovebox techniques.[46] All nondeuterated solvents were purchased from Aldrich and were purified with use of a Glass Contour solvent purification system. The germanes $R_2Ge(NMe_2)CH_2CH_2OEt$ (**5a**: R = Bu; **5b**: R = Et; **5c**: R = Ph) were prepared according to a published procedure[28] and $PhGeH_3$ was prepared by reaction of $PhGeCl_3$ (Gelest, Inc.) with $LiAlH_4$.[47] NMR spectra were recorded on a Varian Gemini 2000 spectrometer operating at 300.0 MHz (^1H), 282.3 (^{19}F), or 75.5 MHz (^{13}C). The ^{19}F NMR spectra were referenced to $C_6H_5CF_3$ set at δ –63.72 ppm while ^1H and ^{13}C NMR spectra were referenced to the C_6D_6 solvent. UV/visible spectra were recorded on a Hewlett-Packard Agilent UV/visible spectroscopy system. Elemental analyses were conducted by Midwest Microlab, LLC (Indianapolis, IN).

Synthesis of $PhGe(GePh_3)_3$ (1). To a solution of $PhGeH_3$ (0.191 g, 1.25 mmol) in acetonitrile (10 mL) was added a solution of Ph_3GeNMe_2[48] (1.31 g, 3.76 mmol) in acetonitrile (20 mL). The reaction mixture was sealed in a Schlenk tube and then heated in an oil bath at 85 °C for 48 h. The reaction mixture was allowed to cool and the solvent was removed in vacuo. Distillation of the crude product mixture (135 °C, 0.01 torr) yielded 1.131 g (85%) of **1** as colorless crystals (mp 264 °C). ^1H NMR (C_6D_6, 25 °C) δ 7.66 (d, J = 7.5 Hz, 2H, o-H $((C_6H_5)_3Ge)_3Ge(C_6\mathit{H}_5)$), 7.26 (d, J = 7.5 Hz, 18H, o-H $((C_6\mathit{H}_5)_3Ge)_3Ge(C_6H_5)$), 7.07 (m, 3H, m-H and p-H $(C_6H_5)_3Ge)_3Ge(C_6\mathit{H}_5)$), 6.94 (m, 27H, m-H and p-H $(C_6\mathit{H}_5)_3Ge)_3Ge(C_6H_5)$) ppm. ^{13}C NMR (C_6D_6, 25 °C) δ 138.9 ($ipso$-$((\mathit{C}_6H_5)_3Ge)_3Ge(C_6H_5)$), 138.6 ($ipso$-$((C_6H_5)_3Ge)_3Ge(\mathit{C}_6H_5)$), 136.6 ($o$-$((\mathit{C}_6H_5)_3Ge)_3Ge(C_6H_5)$), 134.9 ($o$-$((C_6H_5)_3Ge)_3Ge(\mathit{C}_6H_5)$), 128.9 ($p$-$((\mathit{C}_6H_5)_3Ge)_3Ge(C_6H_5)$), 128.6 ($p$-$((C_6H_5)_3Ge)_3Ge(\mathit{C}_6H_5)$), 128.5 ($m$-$((\mathit{C}_6H_5)_3Ge)_3Ge(C_6H_5)$), 128.2 ($m$-$((C_6H_5)_3Ge)_3Ge(\mathit{C}_6H_5)$) ppm. UV/vis ($CH_2Cl_2$): λ_{max} 256 nm ($\epsilon = 5.1 \times 10^4$ L mol^{-1} cm^{-1}). Anal. Calcd. for $C_{60}H_{50}Ge_4$: C, 67.90; H, 4.75. Found: C, 67.43; H, 4.69.

Small-Scale Synthesis of $(F_3CO_2SO)Ge(GePh_3)_3$ (2). To a solution of $(Ph_3Ge)_3GePh$ (**1**) (0.090 g, 0.085 mmol) in $CDCl_3$ (0.5 mL) in a screw-cap NMR tube was added neat triflic acid (7.4 μL, 0.013 g, 0.084 mmol) with a micropipetter. The reaction mixture was kept at room temperature for 4 h, after which time the ^{19}F NMR spectrum of the solution exhibited a single resonance at δ −77.7 ppm indicating complete consumption of $HOSO_2CF_3$ and formation of $(F_3CO_2SO)Ge(GePh_3)_3$ (**2**). The solution was transferred to a conical flask and the volatiles were removed in vacuo to yield 0.082 g (80%) of **2** as a white solid. IR (Nujol mull) 1305 (s, $\upsilon_{as}(SO_3)$), 1261 (m, $\upsilon_{as}(SO_3)$), 1237 (s), 1200 (s, $\upsilon_s(CF_3)$), 1150 (s, $\upsilon_{as}(CF_3)$), 1094 (s), 1024 (m), 998 (m), 937 (s, $\upsilon_s(SO_3)$) cm^{-1}.

Small-Scale Synthesis of $HGe(GePh_3)_3$ (3). The sample of compound **2** was dissolved in Et_2O (5 mL) and treated with a solution of $LiAlH_4$ (0.0039 g, 0.10 mmol) in Et_2O (5 mL). The solution was stirred for 4 h at room temperature and the volatiles were removed in vacuo. The crude product mixture was dissolved in benzene (5 mL) and filtered through Celite. The Celite pad was washed with benzene (3 × 2 mL) and the solvent was removed in vacuo to yield **3** (0.054 g, 64% based on **1**) as a white solid (mp 210 °C). ^1H NMR (C_6D_6, 25 °C) δ 7.26 (d, J = 8.1 Hz, 18H, o-H $((C_6H_5)_3Ge)_3Ge(C_6H_5)$), 7.15–6.92 (m, 27H, m-H and p-H), 5.85 (s, 1H, Ge-H) ppm. ^{13}C NMR (C_6D_6, 25 °C) δ 136.5 ($ipso$-C), 128.8 (o-C), 128.6 (p-C), 127.5 (m-C) ppm. IR (Nujol mull) 1953 cm^{-1} (υ Ge–H). Anal. Calcd for $C_{54}H_{46}Ge_4$: C, 65.83; H, 4.71. Found: C, 65.27; H, 4.62.

Preparative-Scale Synthesis of $HGe(GePh_3)_3$ (3). To a solution of **1** (0.200 g, 0.188 mmol) in CH_2Cl_2 (1.1 mL) was added triflic acid (0.017 mL, 0.029 g, 0.19 mmol) under a stream of N_2. The reaction mixture was sealed in a Schlenk tube and stirred for 4 h. The volatiles were removed in vacuo with use of a water bath to yield a white solid. The ^{19}F NMR in benzene-d_6 exhibited a single line at δ –77.7 ppm. The solid product was dissolved in Et_2O (10 mL) and treated with $LiAlH_4$ (0.0080 g, 0.21 mmol) in Et_2O (5 mL). The reaction mixture was stirred for 18 h at 25 °C and the solvent was removed in vacuo to yield 0.171 g (92%) of **3** as a white solid. The spectral attributes of the product were identical with those described above.

Synthesis of $PhGe(GeBu_2CH_2CH_2OEt)_3$ (4). To a solution of $PhGeH_3$ (0.200 g, 1.31 mmol) in CH_3CN (10 mL) was added a solution of $Bu_2Ge(NMe_2)CH_2CH_2OEt$ (**5a**)[28] (1.195 g, 3.932 mmol) in CH_3CN (30 mL). The reaction mixture was sealed in a Schlenk tube and heated at 85 °C for 72 h. The volatiles were removed in vacuo to yield a viscous yellow oil. The crude product was distilled in a Kugelrohr oven (180 °C, 0.050 torr) to furnish **4** (1.163 g, 95%) as a colorless viscous oil. ^1H NMR (C_6D_6, 25 °C) δ 7.66 (d, J = 6.3 Hz, 2H, o-$C_6\mathit{H}_5$), 7.18–7.08 (m, 3H, m-$C_6\mathit{H}_5$ and p-$C_6\mathit{H}_5$), 3.59 (t, J = 7.2 Hz, 6H, $GeCH_2C\mathit{H}_2O-$), 3.31 (q, J = 7.2 Hz, 6H, $-OC\mathit{H}_2CH_3$), 1.55–1.32 (m, 36H, $-C\mathit{H}_2C\mathit{H}_2C\mathit{H}_2CH_3$), 1.14 (t, J = 7.2 Hz, 18H, $-CH_2CH_2CH_2C\mathit{H}_3$), 0.96 (t, J = 7.2 Hz, 6H, $GeC\mathit{H}_2CH_2O-$), 0.91 (t, J = 7.2 Hz, 9H, $-OCH_2C\mathit{H}_3$) ppm. ^{13}C NMR (C_6D_6, 25 °C) δ 138.4 ($ipso$-C_6H_5), 136.1 (o-C_6H_5), 128.4 (p-C_6H_5), 127.6 (m-C_6H_5), 68.8 ($-O\mathit{C}H_2CH_3$), 65.7 ($-GeCH_2\mathit{C}H_2-$), 28.8 ($GeCH_2CH_2\mathit{C}H_2CH_3$), 27.1 ($Ge\mathit{C}H_2CH_2O-$), 26.9 ($GeCH_2\mathit{C}H_2CH_2CH_3$), 16.8 ($Ge\mathit{C}H_2CH_2CH_2CH_3$), 16.0 ($-OCH_2\mathit{C}H_3$), 13.8 ($GeCH_2CH_2CH_2\mathit{C}H_3$) ppm. Anal. Calcd for $C_{42}H_{86}Ge_4O_3$: C, 54,27; H, 9.33. Found: C, 53.79; H, 9.88.

Synthesis of $PhGe(GeBu_2GeBu_2CH_2CH_2OEt)_3$ (8a). To a solution of **4** (0.280 g, 0.301 mmol) in benzene (25 mL) was added a 1.0 M solution of DIBAL-H in hexanes (0.903 mL, 0.903 mmol). The reaction mixture was refluxed for 24 h and the volatiles were removed in vacuo to yield a thick oil that was dissolved in CH_3CN (25 mL). The resulting solution was treated with $Bu_2Ge(NMe_2)CH_2CH_2OEt$ (**5a**)[28] (0.275 g, 0.905 mmol) in CH_3CN (10 mL) and the reaction mixture was sealed in a Schlenk tube and heated at 85 °C for 48 h. The volatiles were removed in vacuo to yield a thick yellow oil that was eluted through a 1.5 in. × 1.5 in. silica gel column with 40 mL of a 1:20 (v/v) mixture of Et_2O:hexane as the eluent. The volatiles were removed from the eluent in vacuo to furnish **8a** (0.193 g, 43%) as a colorless oil. ^1H NMR (C_6D_6, 25 °C) δ 7.73 (d, J = 7.5 Hz, 2H, o-$C_6\mathit{H}_5$), 7.28–7.17 (m, 3H, m-$C_6\mathit{H}_5$ and p-$C_6\mathit{H}_5$), 3.67 (t, J = 7.8 Hz, 6H, $GeCH_2C\mathit{H}_2O-$), 3.41 (q, J = 6.8 Hz, 6H, $-OC\mathit{H}_2CH_3$), 1.62–1.12 (m, 78 H, $GeC\mathit{H}_2C\mathit{H}_2C\mathit{H}_2CH_3$ and $GeC\mathit{H}_2CH_2O-$), 1.03–0.97 (m, 45 H, $GeCH_2CH_2CH_2C\mathit{H}_3$ and $-OCH_2C\mathit{H}_3$) ppm. ^{13}C NMR (C_6D_6, 25 °C) δ 139.2 ($ipso$-C_6H_5), 136.2 (o-C_6H_5), 128.4 (p-C_6H_5), 128.2 (m-C_6H_5), 68.9 ($-O\mathit{C}H_2CH_3$), 65.8 ($-GeCH_2\mathit{C}H_2-$), 29.0 ($GeCH_2CH_2\mathit{C}H_2CH_3$), 28.8 ($GeCH_2CH_2\mathit{C}H_2CH_3$), 27.3 ($Ge\mathit{C}H_2CH_2O-$), 27.1 ($GeCH_2\mathit{C}H_2CH_2CH_3$), 26.9 ($GeCH_2\mathit{C}H_2CH_2CH_3$), 16.0 ($Ge\mathit{C}H_2CH_2CH_2CH_3$), 15.7 ($Ge\mathit{C}H_2CH_2CH_2CH_3$), 14.8 ($-OCH_2\mathit{C}H_3$), 13.9 ($GeCH_2CH_2CH_2\mathit{C}H_3$ and $GeCH_2CH_2CH_2\mathit{C}H_3$) ppm. Anal. Calcd for $C_{66}H_{140}Ge_7O_3$: C, 53.20; H, 9.47. Found: C, 53.52; H, 9.54.

Synthesis of $PhGe(GeBu_2GeEt_2CH_2CH_2OEt)_3$ (8b). To a solution of **4** (0.370 g, 0.398 mmol) in benzene (20 mL) was added a 1.0 M solution of DIBAL-H in hexanes (1.19 mL, 1.19 mmol). The reaction mixture was heated at reflux for 24 h and the volatiles were removed in vacuo to yield a thick oil that was dissolved in CH_3CN (30 mL). The resulting solution was treated with

---

(47) Meyer, J. M.; Allred, A. L. *J. Phys. Chem.* **1968**, *72*, 3043–3045.

(48) Rivière, P.; Rivière-Baudet, M.; Couret, C.; Satgé, J. *Synth. React. Inorg. Met. Org. Chem.* **1974**, *4*, 295–307.

Table 2. Crystallographic Data for Compound $1 \cdot C_7H_8$

formula	$C_{67}H_{58}Ge_4$
fw (g mol^{-1})	1153.49
cryst size (mm)	0.30 × 0.15 × 0.10
cryst system	monoclinic
space group	$P2_1/c$
a (Å)	12.6857(8)
b (Å)	18.497(1)
c (Å)	23.226(2)
α (deg)	90
β (deg)	98.340(1)
γ (deg)	90
V (Å^3)	5392.1(6)
Z	4
ρ_{calc} (g cm^{-3})	1.421
abs coeff (mm^{-1})	2.250
F(000)	2352
θ range (deg)	1.62 to 27.95
index ranges	$-16 \le h \le 16$, $-23 \le k \le 23$, $-30 \le l \le 30$
no. of reflns collected	49681
no. of independent reflns	12299 ($R_{\mathrm{int}} = 0.0348$)
completeness to $\theta = 25.00°$ (%)	100.0
abs corr	multiscan/APEXII SADABS
max and min transmission	0.8063 and 0.5518
refinement method	full-matrix least squares on F^2
no. of data/resteraints/parameters	12299/0/641
goodness-of-fit on F^2	1.014
temp (K)	173(2)
radiation	Mo Kα
wavelength (Å)	0.71073
R	0.0326
R_{w}	0.0703
largest peak and hole (e Å^{-3})	1.540 and –1.247

$\mathrm{Et_2Ge(NMe_2)CH_2CH_2OEt}$ (**5b**)[28] (0.295 g, 1.19 mmol) in $\mathrm{CH_3CN}$ (15 mL) and the reaction mixture was sealed in a Schlenk tube and heated at 85 °C for 48 h. The volatiles were removed in vacuo to yield a thick colorless oil that was eluted through a 1.5 in. × 1.5 in. silica gel column with 40 mL of a 1:10 (v/v) mixture of $\mathrm{Et_2O}$:hexane as the eluent. The volatiles were removed from the eluent in vacuo and the resulting yellow oil was distilled in a Kugelrohr oven (120 °C, 0.050 torr) to furnish **8b** (0.470 g, 89%) as a pale yellow oil. ^{1}H NMR ($\mathrm{C_6D_6}$, 25 °C) δ 7.72 (d, $J = 6.6$ Hz, 2H, o-$\mathrm{C_6}H_5$), 7.27–7.21 (m, 3H, m-$\mathrm{C_6}H_5$ and p-$\mathrm{C_6}H_5$), 3.36 (t, $J =$ 6.9 Hz, 6H, $-\mathrm{OC}H_2\mathrm{CH_3}$), 3.23 (q, $J = 7.2$ Hz, 6H, $\mathrm{GeCH_2C}H_2\mathrm{O}-$), 1.61–1.39 (m, 24H, $\mathrm{GeCH_2C}H_2\mathrm{C}H_2\mathrm{CH_3}$), 1.31–1.08 (m, 24H, $\mathrm{GeC}H_2\mathrm{CH_2CH_2CH_3}$ and $\mathrm{GeC}H_2\mathrm{CH_3}$), 1.06–0.98 (m, 45H, $\mathrm{GeCH_2CH_2CH_2C}H_3$, $\mathrm{GeCH_2C}H_3$, and $-\mathrm{OCH_2C}H_3$), 0.82 (t, $J = 7.5$ Hz, 6H, $\mathrm{GeC}H_2\mathrm{CH_2O}-$) ppm. ^{13}C NMR ($\mathrm{C_6D_6}$, 25 °C) δ 136.6 ($ipso$-$\mathrm{C_6}H_5$), 136.1 (o-$\mathrm{C_6}H_5$), 128.2 (p-$\mathrm{C_6}H_5$), 127.6 (m-$\mathrm{C_6}H_5$), 67.3($-\mathrm{O}C\mathrm{H_2CH_3}$), 65.9 ($-\mathrm{GeCH_2}C\mathrm{H_2}-$), 28.8 ($\mathrm{GeCH_2CH_2}C\mathrm{H_2CH_3}$), 27.3 ($\mathrm{Ge}C\mathrm{H_2CH_2O}-$), 27.0 ($\mathrm{GeCH_2}C\mathrm{H_2CH_2CH_3}$), 15.9 ($\mathrm{Ge}C\mathrm{H_2CH_2CH_2CH_3}$), 15.3 ($\mathrm{Ge}C\mathrm{H_2CH_3}$), 14.8 ($-\mathrm{OCH_2}C\mathrm{H_3}$), 13.9 ($\mathrm{GeCH_2CH_2CH_2}C\mathrm{H_3}$), 8.6 ($\mathrm{GeCH_2}C\mathrm{H_3}$) ppm. Anal. Calcd for $\mathrm{C_{54}H_{116}Ge_7O_3}$: C, 49.07; H, 8.85. Found: C, 49.42; H, 8.71.

Synthesis of $\mathrm{PhGe(GeBu_2GePh_2CH_2CH_2OEt)_3}$ (8c). To a solution of **4** (0.200 g, 0.215 mmol) in benzene (25 mL) was added a 1.0 M solution of DIBAL-H in hexanes (0.646 mL, 0.646 mmol). The reaction mixture was heated at reflux for 24 h and the volatiles were removed in vacuo to yield a thick oil that was dissolved in $\mathrm{CH_3CN}$ (25 mL). The resulting solution was treated with $\mathrm{Ph_2Ge(NMe_2)CH_2CH_2OEt}$ (**5c**)[28] (0.222 g, 0.645 mmol) in $\mathrm{CH_3CN}$ (10 mL) and the reaction mixture was sealed in a Schlenk tube and heated at 85 °C for 48 h. The volatiles were removed in vacuo to yield a thick yellow oil that was eluted through a 1.5 in. × 1.5 in. silica gel column with 40 mL of a 1:20 (v/v) mixture of $\mathrm{Et_2O}$:hexane as the eluent. The volatiles were removed from the eluent in vacuo and the resulting yellow oil was distilled in a Kugelrohr oven (120 °C, 0.050 torr) to furnish **8c** (0.105 g, 30%) as a pale yellow oil. ^{1}H NMR ($\mathrm{C_6D_6}$, 25 °C) δ 7.74 (d, $J = 6.6$ Hz, 2H, o-$\mathrm{C_6}H_5$ at $\mathrm{Ge_{central}}$), 7.66 (d, $J = 7.5$ Hz, 12H, o-$\mathrm{C_6}H_5$ at $\mathrm{Ge_{peripheral}}$), 7.28–7.14 (m, 21 H, m-$\mathrm{C_6}H_5$ and p-$\mathrm{C_6}H_5$), 3.59 (t, $J = 7.5$ Hz, 6H, $\mathrm{GeCH_2C}H_2\mathrm{O}-$), 3.31 (q, $J = 6.9$ Hz, 6H, $-\mathrm{OC}H_2\mathrm{CH_3}$), 1.54–1.33 (m, 24H, $-\mathrm{CH_2C}H_2\mathrm{C}H_2\mathrm{CH_3}$), 1.22–1.11 (m, 18H, $-\mathrm{C}H_2\mathrm{CH_2CH_2CH_3}$ and $\mathrm{GeC}H_2\mathrm{CH_2O}-$), 0.95 (t, $J = 7.2$ Hz, 9H, $-\mathrm{OCH_2C}H_3$), 0.92 (t, $J =$ 7.2 Hz, 18H $\mathrm{GeCH_2CH_2CH_2C}H_3$) ppm. ^{13}C NMR ($\mathrm{C_6D_6}$, 25 °C) δ 139.5 ($ipso$-$\mathrm{C_6}H_5$), 138.6 ($ipso$-$\mathrm{C_6}H_5$), 136.6 (o-$\mathrm{C_6}H_5$), 136.1 (o-$\mathrm{C_6}H_5$), 128.5 (p-$\mathrm{C_6}H_5$), 128.3 (p-$\mathrm{C_6}H_5$), 127.9 (m-$\mathrm{C_6}H_5$), 127.7 (m-$\mathrm{C_6}H_5$), 68.8 ($-\mathrm{O}C\mathrm{H_2CH_3}$), 65.7 ($-\mathrm{GeCH_2}C\mathrm{H_2}-$), 29.0 ($\mathrm{GeCH_2CH_2}C\mathrm{H_2CH_3}$), 27.2 ($\mathrm{Ge}C\mathrm{H_2CH_2O}-$), 26.9 ($\mathrm{GeCH_2}C\mathrm{H_2CH_2CH_3}$), 15.9 ($\mathrm{Ge}C\mathrm{H_2CH_2CH_2CH_3}$), 14.8 ($-\mathrm{OCH_2}C\mathrm{H_3}$), 13.8 ($\mathrm{GeCH_2CH_2CH_2}C\mathrm{H_3}$) ppm. Anal. Calcd for $\mathrm{C_{78}H_{116}Ge_7O_3}$: C, 58.19; H, 7.26. Found: C, 58.79; H, 7.57.

X-ray Structure Determination for 1. Diffraction intensity data were collected with a Siemens P4/CCD diffractometer. Crystallographic details and details of the X-ray study are shown in Table 2. Absorption corrections were applied for all data by using SADABS. The structure was solved with use of direct methods, completed by difference Fourier synthesis, 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 packaged (G. Sheldrick, Bruker XRD, Madison, WI). The ORTEP diagram was drawn with the ORTEP3 program (L. J. Farrugia, Glasgow).

Acknowledgment. Funding for this work was provided by the Department of Chemistry at Oklahoma State University.

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

OM800040F