Organometallics **2001,** *20,* 4460−4462

Synthesis and Structure of Stable Tri-*tert*-butylgermyl-Substituted Stannylene and Germylene

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Received July 3, 2001

Summary: Significant electron-donating effects of the germyl substituents in the first stable monomeric germyl(aryl)stannylene and germyl(aryl)germylene, which have the sterically encumbering 2,6-dimesitylphenyl group as the aryl substituent, were evidenced by the n → p transition bands appearing at very long wavelengths and the significant downfield shift of the ^{119}Sn NMR resonance in the stannylene.

Although a number of isolable monomeric germylenes and stannylenes have been studied to date,[1] very few of these divalent compounds have electropositive silyl, germyl, and stannyl substituents. Among the known relatively stable *monomeric* stannylenes having the electropositive substituents **1**−**6** (Chart 1),[2] tris(trimethylsilyl)silyl-substituted stannylenes **1** and **2** are equilibrated with their dimers in solution but exist as the dimers in the solid state.[1] Stannylenes **3**−**6** are monomeric in the solid state, but **3** and **4** are coordinated by the neighboring amino nitrogens.[3] No stable germylenes with electropositive substituents have been synthesized until now.

Chart 1

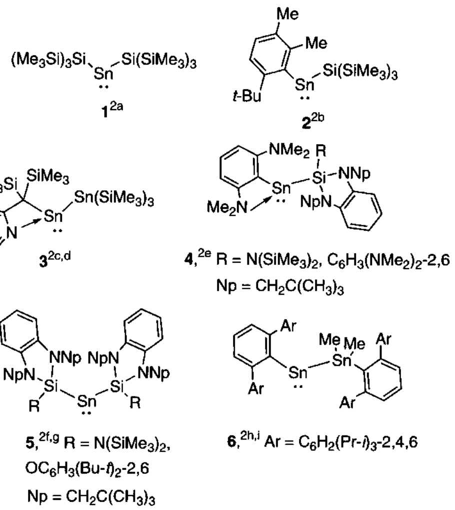
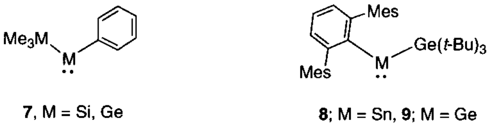


Chart 2



One of the most interesting features of these group 14 metal substituted divalent compounds is the substantial effects of the metal substituents on the electronic structure. Electron-donating substituents such as silyl and germyl groups should raise the n-orbital level and, hence, cause the decrease of the n → p transition energy as well as the singlet−triplet energy difference.[4] Actually, Kira, Maruyama, and Sakurai have reported that matrix-isolated silylsilylenes and silylgermylenes **7** (Chart 2) show a remarkable red shift of the n(Si) → 3p(Si) and n(Ge) → 4p(Ge) transitions.[4a] We report herein the synthesis and properties of the first stable monomeric germylstannylene **8** and germylgermylene **9**, which have the sterically encumbering 2,6-dimesitylphenyl group developed by Power et al.[5] Remarkable electron-donating effects of a germyl group on the electronic nature of germylene and stannylene have been revealed by UV−vis and NMR spectra of **8** and **9**.

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(1) For recent reviews of isolable divalent species of Ge, Sn, and Pb, see: (a) Barrau, J.; Escudié, J.; Satgé, J. *Chem. Rev.* **1990**, *90*, 283. (b) Lappert, M. F. *Coord. Chem. Rev.* **1990**, *100*, 267. (c) Neumann, W. P. *Chem. Rev.* **1991**, *91*, 311. (d) Lappert, M. F. *Main Group Met. Chem.* **1994**, *17*, 183. (e) Barrau, J.; Rima, G. *Coord. Chem. Rev.* **1998**, *178*−*180*, 593.

(2) (a) Klinkhammer, K. W.; Schwarz, W. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1334. (b) Stürmann, M.; Saak, W.; Klinkhammer, K. W.; Weidenbruch, M. *Z. Anorg. Allg. Chem.* **1999**, *625*, 1955. (c) Cardin, C. J.; Cardin, D. J.; Constantine, S. P.; Todd, A. K.; Teat, S. J.; Coles, S. *Organometallics* **1998**, *17*, 2144. (d) Benet, S.; Cardin, C. J.; Cardin, D. J.; Constantine, S. P.; Heath, P.; Rashid, H.; Teixeira, S.; Thorpe, J. H.; Todd, A. K. *Organometallics* **1999**, *18*, 389. (e) Drost, C.; Gehrhus, B.; Hitchcock, P. B.; Lappert, M. F. *Chem. Commun.* **1997**, 1845. (f) Gehrhus, B.; Hitchcock, P. B.; Lappert, M. F. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 2514. (g) Gehrhus, B.; Hitchcock, P. B.; Lappert, M. F. In *Organosilicon Chemistry IV*; Auner, N., Weis, J., Eds.; Wiley-VCH: Weinheim, Germany, 2000; p 84. (h) Eichler, B. E.; Power, P. P. *Inorg. Chem.* **2000**, *39*, 5444. (i) Eichler, E.; Phillips, B. L.; Power, P. P.; Augustine, M. P. *Inorg. Chem.* **2000**, *39*, 5450.

(3) Stannylenes **5** and their Pb analogue were confirmed by X-ray crystallography to be monomeric in the solid state without intramolecular coordiantion by heteroatom substituents.[2f,g] However, no convincing NMR data in solution were given for **5**. At present, only **6** is known to be a monomeric dicoordinate Sn(II) compound with electropositive substituents both in solution and in the solid state.

(4) Remarkable effects of the electropositive metallic substituents on the electronic structure of silylenes have been well documented. Theoretical studies: (a) Grev, R. S.; Schaefer, H. F., III; Gaspar, P. P. *J. Am. Chem. Soc.* **1991**, *113*, 5638. (b) Apeloig, Y.; Karni, M.; West, R.; Welsh, K. *J. Am. Chem. Soc.* **1994**, *116*, 9719. (c) Holthausen, M. C.; Koch, W.; Apeloig, Y. *J. Am. Chem. Soc.* **1999**, *121*, 2623. Experimental studies: (d) Kira, M.; Maruyama, T.; Sakurai, H. *Chem. Lett.* **1993**, 1345; XXV Silicon Symposium, Los Angeles, April 1992; paper 72P. (e) Banks, K. E.; Wang, Y.; Conlin, R. T. XXV Silicon Symposium, Los Angeles, April 1992; paper 7.

10.1021/om010591h CCC: $20.00
Publication on Web 10/03/2001

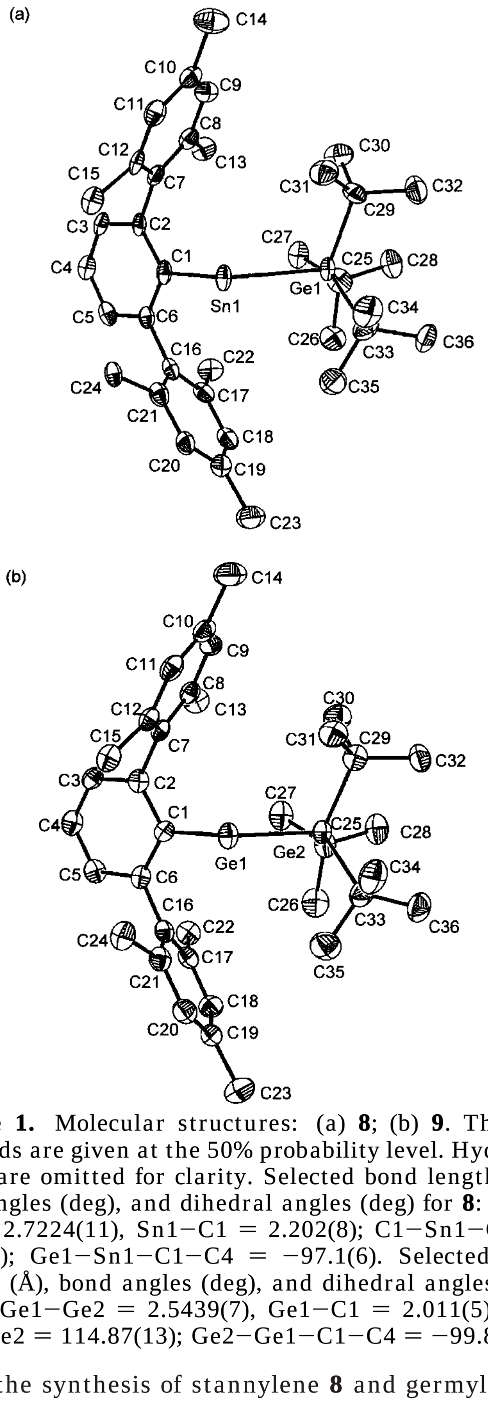
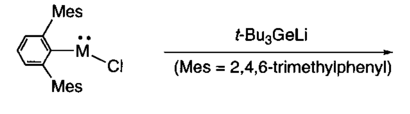


Figure 1. Molecular structures: (a) **8**; (b) **9**. Thermal ellipsoids are given at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å), bond angles (deg), and dihedral angles (deg) for **8**: Sn1−Ge1 = 2.7224(11), Sn1−C1 = 2.202(8); C1−Sn1−Ge1 = 112.7(2); Ge1−Sn1−C1−C4 = −97.1(6). Selected bond lengths (Å), bond angles (deg), and dihedral angles (deg) for **9**: Ge1−Ge2 = 2.5439(7), Ge1−C1 = 2.011(5); C1−Ge1−Ge2 = 114.87(13); Ge2−Ge1−C1−C4 = −99.8(3).

For the synthesis of stannylene **8** and germylene **9**, we have found that the direct reactions of (tri-*tert*-butylgermyl)lithium[6] with the corresponding arylchlorostannylene **10**[7] and arylchlorogermylene **11**,[7] respectively, in a hydrocarbon solvent are useful as shown in eq 1. Compounds **8** and **9**[8] are obtained in 29 and 9% yields, respectively, as blue crystals.



10; M = Sn, **11**; M = Ge

8 and 9 (1)

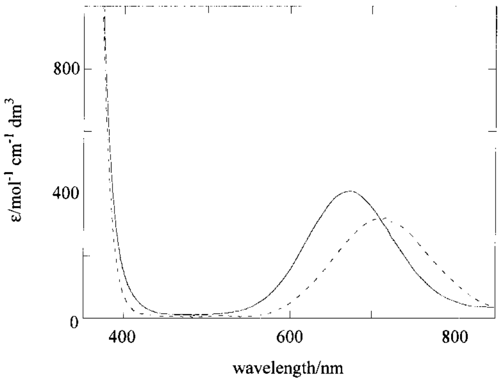


Figure 2. UV−vis spectra of **8** (solid line) and **9** (dashed line) in 3-methylpentane at room temperature.

Molecular structures of germylstannylene **8** and germylgermylene **9** determined by X-ray crystallography are shown in Figure 1.[9] Stannylene **8** and germylene **9** are monomeric in the solid state; the shortest intermolecular distances between two Sn(II) atoms in **8** and between two Ge(II) atoms in **9** are 9.08 and 9.14 Å, respectively, in the crystals. The $\mathrm{Sn^{II}}$−C(Ar) bond length of **8** (2.202(8) Å) is slightly shorter than those of known stable diarylstannylenes: 2.225(4) and 2.267(4) Å for **12**[10] and 2.225(5) Å for **14a**[7] in Chart 3. The shortening of the $\mathrm{Sn^{II}}$−C(Ar) distance may be ascribed to an effective σ−π conjugation between the Ge−Sn bond and the aromatic p system; the dihedral angle between the Ge−Sn σ bond and the pπ orbital at C(Ar) is 7°, to allow the effective σ−π conjugation. A slightly longer $\mathrm{Sn^{II}}$−C(Ar) bond length for aryl(stannyl)stannylene **6** (2.227(2) Å)[2h] as compared to that of **8** may be the result of the greater steric congestion in the former. The $\mathrm{Sn^{II}}$−$\mathrm{Ge^{IV}}$ bond length of **1** is 2.7224(11) Å, which is the first determination of $\mathrm{Sn^{II}}$−$\mathrm{Ge^{IV}}$ bond length. The structural feature of germylene **9** resembles basically that of **8**. $\mathrm{Ge^{II}}$−C(Ar) and $\mathrm{Ge^{IV}}$−$\mathrm{Ge^{II}}$ bond lengths are 2.011(5) and 2.5439(7) Å, respectively.

The UV−vis absorption spectra of **8** and **9** in 3-methylpentane are shown in Figure 2. The characteristic n → p absorption band maxima of **8** and **9** were observed at 673 nm (ϵ 400) and 719 nm (ϵ 340), respectively, in good accord with the maximum for stannylstannylene

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[5] (a) Power, P. P. *Chem. Rev.* **1999**, *99*, 3463. (b) Twamley, B.; Haubrich, S. T.; Power, P. P. *Adv. Organomet. Chem.* **2000**, *44*, 1 and references therein. (c) Clyburne, J. A. C.; McMullen, N. *Coord. Chem. Rev.* **2000**, *210*, 73.

[6] Sekiguchi, A.; Yamazaki, H.; Kabuto, C.; Sakurai, H.; Nagase, S. *J. Am. Chem. Soc.* **1995**, *117*, 8025.

[7] Simons, R. S.; Pu, L.; Olmstead, M. M.; Power, P. P. *Organometallics* **1997**, *19*, 1920.

[8] Synthesis of **8**: a solution of (tri-*tert*-butylgermyl)lithium (1.07 mmol) in tetrahydrofuran (2 mL) was added to a solution of **10** (500 mg, 1.07 mmol) in toluene (20 mL) at room temperature. After the mixture was stirred for 12 h, the volatile materials were removed under reduced pressure. The residual solid was extracted with hexane, filtered through Celite, and concentrated to incipient crystallization. Storage in a −20 °C freezer gave blue crystals of **8** (210 mg, 29% yield). Mp: 160 °C dec. ^{1}H NMR (300 MHz, C_6D_6, 298 K): δ 1.17 (s, 27 H), 2.06 (s, 6 H), 2.28 (s, 6 H), 2.54 (s, 6 H), 6.57 (s, 2 H), 6.75 (s, 2 H), 7.10 (d, $J = 7.6$ Hz, 2 H), 7.37 (t, $J = 7.6$ Hz, 1 H). ^{13}C NMR (75 MHz, C_6D_6, 298 K): δ 21.0, 21.5, 22.3, 33.2, 36.9, 128.4, 129.5, 129.8, 130.4, 134.1, 136.4, 136.7, 137.4, 145.9, 179.7. ^{119}Sn NMR (112 MHz, C_6D_6, 298 K): δ 2960. MS (EI, 70 eV): *m*/*z* 676 (M^+, 20), 433 ($ArSn^+$, 100), 314 (Ar^+, 85). UV−vis (3-methylpentane): λ_{max} (ϵ) 673 nm (400). Anal. Calcd for $C_{36}H_{52}GeSn$: C, 63.95; H, 7.75. Found: C, 63.78; H, 7.58. Germylgermylene **9** was synthesized using a procedure similar to the synthesis of **8**. **9**: blue crystals; 9% yield. mp 167 °C dec. ^{1}H NMR (300 MHz, C_6D_6, 298 K): δ 1.10 (s, 27 H), 2.06 (s, 6 H), 2.27 (s, 6 H), 2.50 (s, 6 H), 6.56 (s, 2 H), 6.75 (s, 2 H), 7.00 (d, $J = 7.6$ Hz, 2 H), 7.31 (t, $J = 7.6$ Hz, 1 H). ^{13}C NMR (75 MHz, C_6D_6, 298 K): δ 20.9, 22.4, 32.6, 34.7, 128.3, 129.0, 129.6, 130.2, 135.2, 135.9, 136.7, 137.9, 140.9, 169.4. MS (EI, 70 eV): *m*/*z* 630 (M^+, 5), 573 ($M^+ -$ *t*-Bu, 25), 387 ($ArGe^+$, 100), 57 (*t*-Bu^+, 40). UV−vis (3-methylpentane): λ_{max} (ϵ) 719 nm (340). Anal. Calcd for $C_{36}H_{52}Ge_2$: C, 68.63; H, 8.32. Found: C, 68.35; H, 8.16.

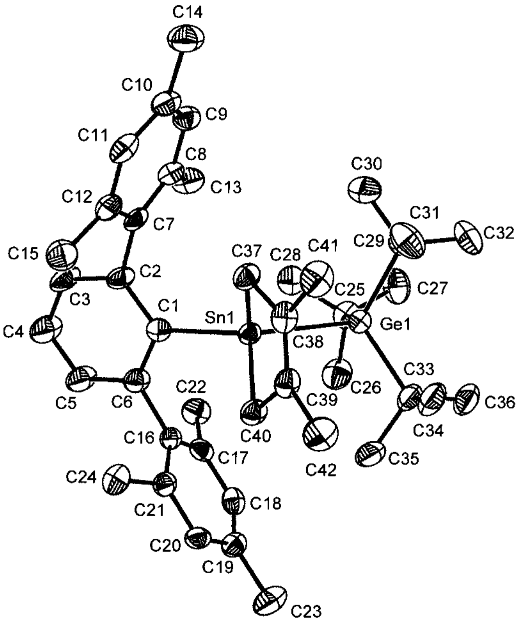
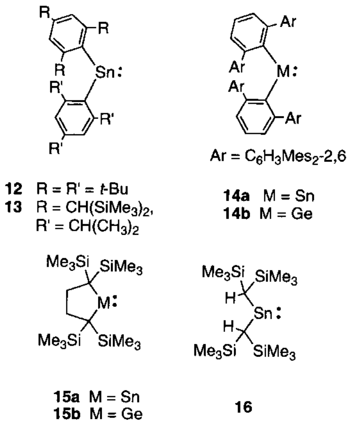


Figure 3. Molecular structure of **17**. Thermal ellipsoids are given at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and bond angles (deg): Sn1−Ge1 = 2.7069(7), Sn1−C1 = 2.218(5); C1−Sn1−Ge1 = 125.69(12).

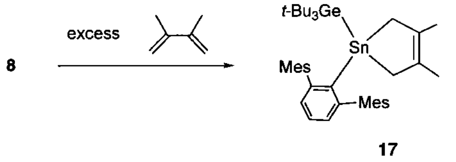
Chart 3



6 observed at 689 nm (ϵ 271).[2h] These bands are significantly red-shifted compared with those of other stable stannylenes and germylenes;[10−12] maxima for stannylenes **14a**[7] and **15a**[11a] are reported to be 553 and 484 nm, respectively, and those for germylenes **14b**[7] and **15b**[11b] are 578 and 450 nm, respectively. The significant red shift is quite parallel to the absorption maximum of matrix-isolated phenyl(trimethylsilyl)germylene (**7**; M = Ge),[4a] which shows the maximum at 610 nm, being 170 nm red-shifted from that of phenylmethylgermylene (440 nm).[13] The present results constitute the first observation of the significant electron-donating effects of metallic substituents in isolable group 14 divalent compounds on the UV−vis spectra. The UV−vis spectra of **8** and **9** show no temperature dependence, indicating that there is no equilibrium between the monomeric species and its dimer in solution.

The significant electron-donating effects of the germyl substituent were also observed in the ^{119}Sn NMR of stannylene **8**. The ^{119}Sn resonance of **8** appeared at 2960 ppm in benzene-d_6, which is similar to that of **6** (2856.9 ppm)[2h,i] but at much lower field than those of other dicoordinate Sn(II) compounds. The ^{119}Sn resonance of **8** is more than 600 ppm lower than the resonances for dialkylstannylenes **15a**[11a] and **16**[14] and diarylstannylene **13**[12a] (Chart 3), which are reported to be 2323, 2315, and 2208 ppm, respectively. The remarkable downfield shift of the ^{119}Sn resonances in **8** and **6** should be ascribed to the larger paramagnetic shielding[2h,i] due to the electron-donating effect of a group 14 metal substituent, which causes the lowering of the n → p excitation energy as observed in the UV−vis spectrum (vide supra).

Expectedly, germylstannylene **8** reacted with 2,3-dimethylbutadiene to give the corresponding adduct **17** (eq 2),[15] which was no longer air and moisture sensitive.



(2)

The structure of **17** was determined by NMR spectroscopy and X-ray crystallography;[16] the molecular structure in the solid state is shown in Figure 3.

Supporting Information Available: Tables and figures giving X-ray structural information on **8**, **9**, and **17**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(9) X-ray crystallographic analysis of **8** and **9**: diffraction data were collected from single crystals of dimensions 0.4 × 0.2 × 0.2 mm (**8**) and 0.2 × 0.2 × 0.1 mm (**9**) in sealed grass capillaries on a Bruker SMART 1k CCD system using graphite-monochromatized Mo Kα radiation (λ = 0.710 69 Å). Crystal data for **8** (120 K): $C_{36}H_{52}GeSn$, FW = 676.06, monoclinic, space group $P2_1/n$, a = 11.1470(19) Å, b = 18.340(3) Å, c = 16.130(3), β = 91.362(3)°, V = 3296.7(10) Å^3, density (calculated) 1.362 Mg/m^3, Z = 4, final R indices (all data) R1 = 0.0781 and wR2 = 0.2088 for 4563 unique reflections. Crystal data for **9** (120 K): $C_{36}H_{52}Ge_2$, FW = 629.96, monoclinic, space group $P2_1/n$, a = 10.9715(10) Å, b = 18.4450(16) Å, c = 16.3004(14) Å, β = 90.979(2)°, V = 3298.2(5) Å^3, density (calculated) 1.269 Mg/m^3, Z = 4, final R indices (all data) R1 = 0.0749 and wR2 = 0.1249 for 4881 unique reflections.

(10) Weidenbruch, M.; Schlaefke, J.; Schafer, A.; Peters, K.; von Schnering, H. G.; Marsmann, H. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1846.

(11) (a) Kira, M.; Yauchibara, R.; Hirano, R.; Kabuto, C.; Sakurai, H. *J. Am. Chem. Soc.* **1991**, *113*, 7785. (b) Kira, M.; Ishida, S.; Iwamoto, T.; Ichinohe, M.; Kabuto, C.; Ignatovich, L.; Sakurai, H. *Chem. Lett.* **1999**, 263.

(12) (a) Tokitoh, N.; Saito, M.; Okazaki, R. *J. Am. Chem. Soc.* **1993**, *115*, 2065. (b) Tokitoh, N.; Manmaru, K.; Okazaki, R. *Organometallics* **1994**, *13*, 167.

(13) Ando, W.; Itoh, H.; Tsumuraya, T. *Organometallics* **1989**, *8*, 2759.

(14) Zilm, K. W.; Lawless, G. A.; Merrill, R. M.; Millar, J. M.; Webb, G. G. *J. Am. Chem. Soc.* **1987**, *109*, 7236.

(15) 2,3-Dimethylbutadiene (1 mL, excess) was added to a solution of **8** (30 mg, 0.04 mmol) in benzene (1 mL) at room temperature. After the mixture was stirred for 12 h, the volatile materials were removed under reduced pressure. Recrystallization from ethanol gave **17** as colorless crystals quantitatively. **17**: mp 147−148 °C. ^{1}H NMR (300 MHz, C_6D_6, 298 K): δ 1.09 (s, 27 H), 1.7−1.8 (m, 4 H), 1.78 (s, 6 H), 2.13 (s, 12 H), 2.17 (s, 6 H), 6.7−6.9 (m, 3 H), 7.11 (s, 4 H). ^{13}C NMR (75 MHz, C_6D_6, 298 K): δ 20.8, 21.2, 22.4, 30.8, 31.9, 32.5, 128.3, 128.4, 129.3, 132.0, 136.3, 136.6, 142.0, 143.3, 150.4. ^{119}Sn NMR (112 MHz, C_6D_6, 298 K): δ −115.7. MS (EI, 70 eV): m/z 758 (M$^+$, 3), 701 (M$^+$ − 57, 5), 676 (M$^+$ − diene, 10), 433 (ArSn$^+$, 40), 314 (Ar$^+$, 100). Anal. Calcd for $C_{42}H_{62}GeSn$: C, 66.53; H, 8.24. Found: C, 66.14; H, 7.98.

(16) Diffraction data were collected from a single crystal of dimensions 0.5 × 0.2 × 0.2 mm. Crystal data for **17** (120 K): $C_{42}H_{64}GeSn$, FW = 758.20, triclinic, space group $P\bar{1}$, a = 11.503(2) Å, b = 15.748(2) Å, c = 21.351(3) Å, α = 91.260(2)°, β = 95.308(2)°, γ = 94.727(3)°, V = 3836.5(9) Å^3, density (calcd) 1.313 Mg/m^3, Z = 4, final R indices (obsd data) R1 = 0.0486, wR2 = 0.1228 for 10 254 unique reflections with $I > 2\sigma(I)$.