Organometallics **2003,** *22,* 5212−5216

Reaction Modes of a Tetragermabutadiene: Cycloadditions versus Ge−Ge Bond Cleavages[1]

Gerhard Ramaker, Wolfgang Saak, Detlev Haase, and Manfred Weidenbruch*

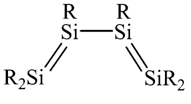
Institut für Reine und Angewandte Chemie, Universität Oldenburg,
Carl-von-Ossietzky-Strasse 9-11, D-26111 Oldenburg, Germany

Received August 22, 2003

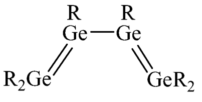
Treatment of hexakis(2,4,6-triisopropylphenyl)tetragermabuta-1,3-diene (**2**) with selenium in the presence of Et_3P furnishes a selenatetragermacyclopentene derivative with an endocyclic Ge−Ge double bond. With small amounts of water **2** reacts to afford an oxatetragermacyclopentane, analogous to THF. The reaction of **2** with Et_3PTe proceeds by cleavage of all Ge−Ge bonds to yield a 1,2,4,5-tetratellura-3,6-digermacyclohexane derivative together with small amounts of the "double-decker" compound $R_4Ge_4Te_6$, R = 2,4,6-$i$$Pr_3C_6H_2$, and a telluradigermirane. In the reaction of **2** with 2-methoxyphenyl isocyanide one Ge−Ge double bond is cleaved to give the 4(1*H*)-trigermatimine ring system with an endocyclic Ge−Ge double bond and the known tetrakis(2,4,6-triisopropylphenyl)digermene (**10**). All new compounds were characterized by X-ray crystallography. Redetermination of the structure of **10** revealed two independent molecules with Ge═Ge bond lengths of 2.2894(6) and 2.2635(14) Å, respectively.

Introduction

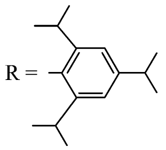
We recently prepared the compounds **1**[2] and **2**[3] as the first molecules containing conjugated Si═Si and Ge═Ge double bonds, respectively. Starting from a tetraaryldisilene, compound **1** was obtained by a sequence of metalation, halogenation, and intermolecular coupling reactions[2] and has since been characterized by 1,2- and 1,4-additions as well as cycloaddition reactions.[4]



1



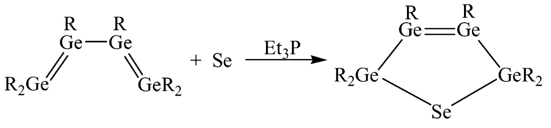
2



Compound **2** is accessible from a tetraaryldigermene by an analogous sequence of reactions. Although **1** is formed in yields up to 60%; the synthesis of **2** requires tedious separation steps and furnishes a maximum yield of 11%. Very recently we have found that the tetragermabutadiene **2** is easily accessible by the reaction of an aryl-Grignard compound with $GeCl_2$·dioxane and magnesium. Although the yield of this synthetic route still only amounts to about 30%, the one-pot procedure does allow the isolation of **2** on a gram scale from readily accessible or commercially available starting materials and thus makes investigations of the reactions of **2** possible.[5] For example, reaction of **2** with dry air yielded a bicyclic compound, which was presumably formed by [4+2] and [2+2] cycloaddition reactions of oxygen to the multiple bonds of **2**, followed by rearrangement reactions of the two O−O bonds. With sulfur a thiatetragermacyclopentene derivative was obtained in high yield.[5] We now report on the reactions of **2** with selenium and tellurium in the presence of Et_3P, with water, and with an aryl isocyanide, which proceed by cycloaddition or addition reactions or by cleavage of Ge−Ge bonds of **2**.

Results and Discussion

Longer heating of **2** with excess selenium in the presence of a small amount of triethylphosphane as a chalcogene transfer reagent furnished yellow crystals of the selenatetragermacyclopentene **3** that were isolated in 67% yield (eq 1).



2 **3** (1)

An X-ray structure analysis of **3** (Figure 1) revealed the presence of an almost planar five-membered ring (sum of endocyclic angles: 537.7°). With an average value of 2.465 Å the Ge(1)−Ge(2) and Ge(3)−Ge(4) bonds are of a typical size for Ge−Ge single bonds. The Ge═Ge double bond length of 2.2975(5) Å is somewhat longer than the corresponding bond in the sulfur-containing five-membered ring (2.2841 Å).[5] Like most other digermenes, compound **3** shows *trans*-bending of the substituents referred to the Ge(2)−Ge(3) vector, which, in this case, is very pronounced with values of 33.4° at Ge(2) and 35.1° at Ge(3).

---

*Corresponding author.

[1] Compounds of Germanium, Tin, and Lead. Part 44. Part 43: Stabenow, F.; Saak, W.; Marsmann, H.; Weidenbruch, M. *J. Am. Chem. Soc.* **2003**, *125*, 10172.

[2] Weidenbruch, M.; Willms, S.; Saak, W.; Henkel, G. *Angew. Chem.* **1997**, *109*, 2612; *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 2503.

[3] Schäfer, H.; Saak, W.; Weidenbruch, M. *Angew. Chem.* **2000**, *112*, 3847; *Angew. Chem., Int. Ed.* **2000**, *39*, 3703.

[4] For recent reviews see: (a) Weidenbruch, M. *J. Organomet. Chem.* **2002**, *646*, 39. (b) Weidenbruch, M. *Organometallics* **2003**, *22*, 4348.

[5] Ramaker, G.; Schäfer, A.; Saak, W.; Weidenbruch, M. *Organometallics* **2003**, *22*, 1302.

10.1021/om034123e CCC: $25.00

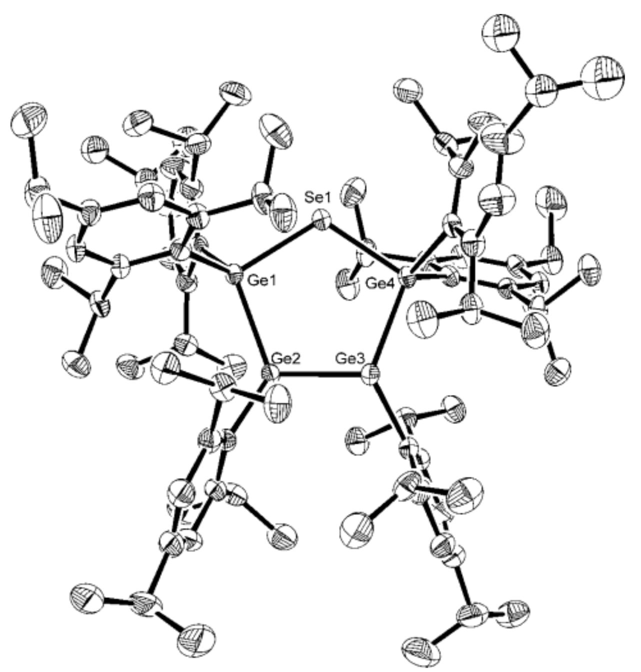
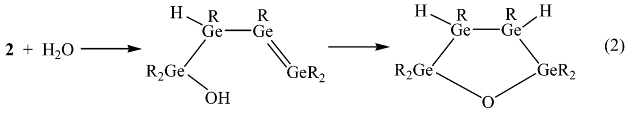


Figure 1. Molecule of **3** in the crystal (hydrogen atoms omitted). Ellipsoids are drawn at 50% probability. Selected bond lengths (Å) and bond angles (deg): Ge(1)−Ge(2) = 2.4567(5), Ge(2)−Ge(3) = 2.2975(5), Ge(3)−Ge(4) = 2.4755(5), Ge(1)−Se = 2.4014(5), Ge(4)−Se = 2.3921(5), Ge(1)−Ge(2)−Ge(3) = 110.064(18), Ge(2)−Ge(3)−Ge(4) = 109.406(19), Ge(3)−Ge(4)−Se = 102.112(18), Ge(4)−Se−Ge(1) = 113.758(18), Se−Ge(1)−Ge(2) = 102.357(18).

The reaction of **2** with selenium closely resembles the analogous reactions of **1** with sulfur, selenium, and tellurium[6] as well as the reaction of **2** with sulfur.[5] The reactions of **1**[7] and **2** with water also proceed similarly and lead to saturated five-membered ring compounds (eq 2).



4 **5**

We may assume that the reaction of **2** with water involves an initial 1,2-addition to one of the Ge−Ge double bonds with subsequent 1,3-hydride shift and ring closure. The X-ray crystallographic analysis (Figure 2) not only confirmed the structure of the oxatetragermacyclopentane **5** but also revealed some interesting features. The formation of a tetragermanediole followed by condensation can probably be excluded, since a similar reaction of a tetrasilanediole was not observed even under harsh conditions.[7]

The large twisting of the ring skeleton of **5** is reflected in the sum of the endocyclic angles of 509° as well as in the differing Ge−Ge bond lengths. Although the Ge(2)−Ge(3) and Ge(3)−Ge(4) bonds with an average value of 2.46 Å are in the typical range for Ge−Ge single bonds, the Ge(1)−Ge(2) bond is markedly stretched with a length of 2.55 Å. The same twisting was observed for the silicon analogue of **5**.

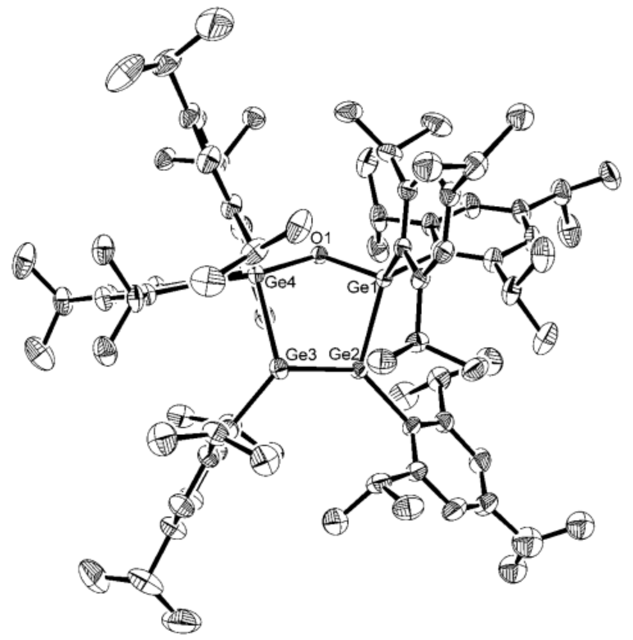
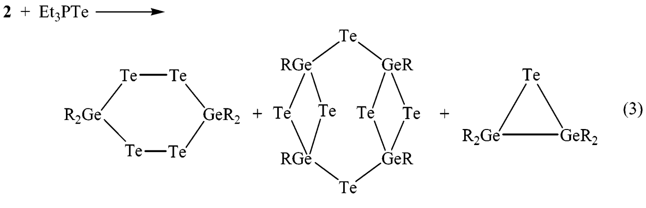


Figure 2. Molecule of **5** in the crystal (hydrogen atoms omitted). Ellipsoids are drawn at 50% probability. Selected bond lengths (Å) and bond angles (deg): Ge(1)−Ge(2) = 2.5494(4), Ge(2)−Ge(3) = 2.4551(5), Ge(3)−Ge(4) = 2.4691(4), Ge(1)−O = 1.8183(19), Ge(4)−O = 1.8319(19), Ge(1)−O−Ge(4) = 126.01(9), O−Ge(1)−Ge(2) = 104.01(12), Ge(1)−Ge(2)−Ge(3) = 93.480(14), Ge(2)−Ge(3)−Ge(4) = 93.895(15), O−Ge(4)−Ge(3) = 91.53(6).

The reactions of selenium and water with **2** proceed in analogy with the corresponding reactions of the tetrasilabutadiene **1**. In contrast, the reaction with tellurium in the presence of triethylphosphane does not lead to the expected unsaturated five-membered ring compound but rather proceeds with cleavage of all Ge−Ge bonds in **2**. Isolated from the complex reaction mixture first, in 15% yield, were light red crystals of a compound identified by X-ray crystallography (Figure 3) as the 1,2,4,5-tetratellura-3,6-digermacyclohexane **6** (eq 3).



6 **7** **8**

The skeletal atoms of the novel ring system **6** comprise a highly folded six-membered ring (sum of endocyclic angles: 625°) in the twist conformation.

In addition to **6**, a few red crystals of another compound that could only be characterized by X-ray crystallography (Figure 4) were isolated. This proved to be the germanium sesquitelluride **7**, having a “double-decker”-type structure with two four-membered rings and two eight-membered rings. The two four-membered rings are planar (sum of angles: 359.7°) and are perpendicular to the common plane of the eight-

---

(6) Grybat, A.; Boomgaarden, S.; Saak, W.; Marsmann, H.; Weidenbruch, M. *Angew. Chem.* **1999**, *111*, 2161; *Angew. Chem., Int. Ed.* **1999**, *38*, 2010.

(7) Willms, S.; Grybat, A.; Saak, W.; Weidenbruch, M.; Marsmann, H. *Z. Anorg. Allg. Chem.* **2000**, *626*, 1148.

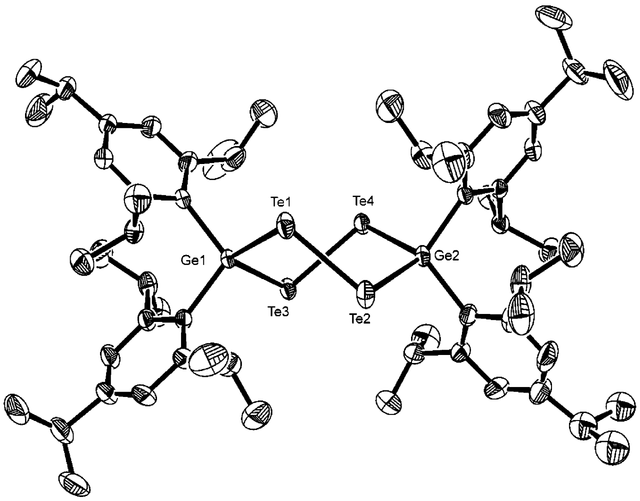


Figure 3. Molecule of **6** in the crystal (hydrogen atoms omitted). Ellipsoids are drawn at 50% probability. Selected bond lengths (Å) and bond angles (deg): Ge(1)−Te(1) = 2.5846(5), Te(1)−Te(2) = 2.7078(4), Te(2)−Ge(2) = 2.6005(5), Ge(2)−Te(4) = 2.5994(5), Te(3)−Te(4) = 2.7077(4), Te(1)−Ge(1)−Te(3) = 106.278(15), Ge(1)−Te(3)−Te(4) = 102.793(13), Te(3)−Te(4)−Ge(2) = 104.458(13), Te(4)−Ge(2)−Te(2) = 105.900(15), Ge(2)−Te(2)−Te(1) = 102.241(14), Te(2)−Te(1)−Ge(1) = 103.553(14).

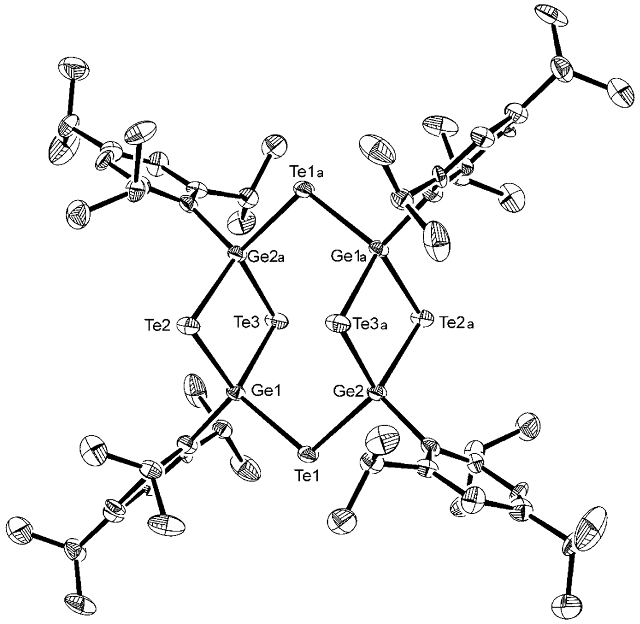


Figure 4. Molecule of **7** in the crystal (hydrogen atoms omitted). Ellipsoids are drawn at 50% probability. Selected bond lengths (Å) and bond angles (deg): Te(1)−Ge(1) = 2.5924(9), Te(1)−Ge(2) = 2.5796(8), Ge(1)−Te(2) = 2.5899(9), Ge(1)−Te(3) = 2.5887(9), Te(2)−Ge(2a) = 2.5988(10), Te(3)−Ge(2a) = 2.5885(9), Ge(1)−Te(1)−Ge(2) = 106.65(3), Ge(1)−Te(2)−Ge(2a) = 85.27(3), Ge(1)−Te(3)−Ge(2a) = 85.52(3), Te(2)−Ge(2a)−Te(3) = 94.34(3), Te(2)−Ge(1)−Te(3) = 94.57(3).

membered rings. A similar structure has been observed previously only for the sulfur compound ($(t\text{BuGe})_4S_6$).[8]

The additionally obtained yellow crystals of the telluradigermirane **8** were also only characterizable by X-ray crystallography (Figure 5). However, this ring system is not new. Ando et al. had previously reported the preparation of an analogous compound by addition of tellurium to a tetraaryldigermene.[9]

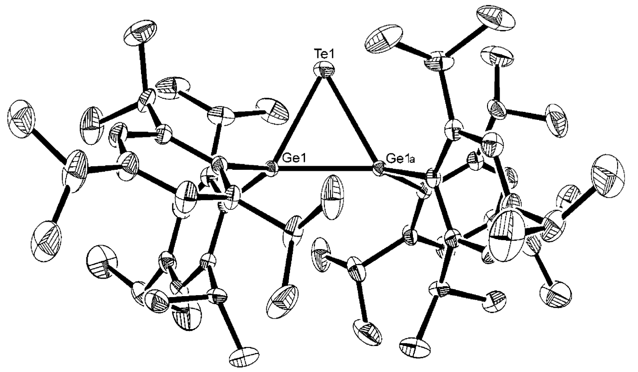
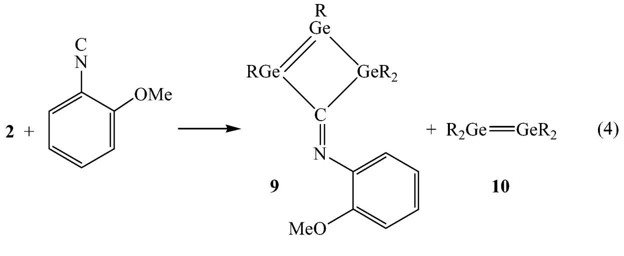


Figure 5. Molecule of **8** in the crystal (hydrogen atoms omitted). Ellipsoids are drawn at 50% probability. Selected bond lengths (Å) and bond angles (deg): Ge(1)−Te = 2.6107(3), Ge(1)−Ge(1a) = 2.4694(5), Ge(1)−Te−Ge(1a) = 56.452(12), Ge(1)−Ge(1a)−Te = 61.774.

The differing reactivity of tellurium toward compounds **1** and **2** is probably due to the following factors. In contrast to the lighter chalcogens, tellurium reacts much more slowly with the multiple bonds in **1** and **2**, thus making longer reaction times and higher temperatures necessary. Although the Si═Si bonds in **1** are stable under these conditions, the Ge═Ge bonds in **2**—in analogy with the behavior of other digermenes—probably dissociate at least in part to afford germylenes on account of the low bond dissociation energy. Subsequent cleavage reactions of the remaining Ge_3R_4 fragment would then explain the palette of products formed.

The assumption of an initial germylene cleavage is impressively confirmed by the reaction of **2** with 2-methoxyphenyl isocyanide. The dark red crystals isolated in 59% yield from this reaction were identified as the four-membered ring compound **9** on the basis of analytical data and an X-ray crystallographic analysis (Figure 6). In addition, the digermene **10** resulting from dimerization of the germylene was also obtained (eq 4).



(4)

The four-membered ring of **9** is practically planar with a sum of endocyclic angles of 358.9°. The Ge═Ge bond length is in the region typical for digermenes. It is not clear whether the neighboring Ge═Ge and C═N double bonds are in conjugation to each other. The absorption maximum in the electronic spectrum occurs in about the same region as that of, for example, compound **10**,[11] which seems not to support conjugation. On the other hand, the dark red color of **9** as well as the absorptions reaching far into the red region do suggest a bathochromic shift due to conjugation. The situation is apparently

---

(8) Ando, W.; Kadowaki, T.; Kabe, Y.; Ishii, M. *Angew. Chem.* **1992**, *104*, 84; *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 59.

(9) Tsumuraya, T.; Kabe, Y.; Ando, W. *J. Chem. Soc., Chem. Commun.* **1990**, 1159.

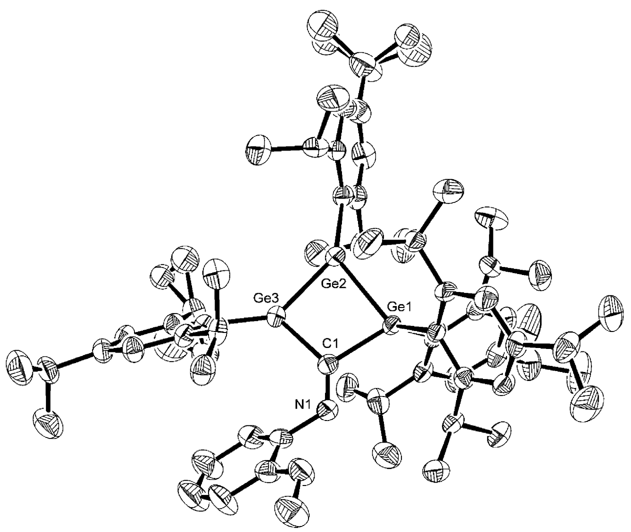


Figure 6. Molecule of **9** in the crystal (hydrogen atoms omitted). Ellipsoids are drawn at 50% probability. Selected bond lengths (Å) and bond angles (deg): Ge(1)−Ge(2) = 2.4297(8), Ge(2)−Ge(3) = 2.2808(7), Ge(1)−C(1) = 2.028(5), Ge(3)−C(1) = 1.999(5), C(1)−N = 1.269(6), Ge(1)−Ge(2)−Ge(3) = 83.70(2), Ge(2)−Ge(3)−C(1) = 88.40(14), Ge(3)−C(1)−Ge(1) = 102.7(2), C(1)−Ge(1)−Ge(2) = 83.75(15).

less ambiguous in a five-membered ring system with neighboring Si═Ge and C═C double bonds in which no conjugation is observed between these bonds.[12]

The digermene **10** also obtained in this reaction has been known for some time[10,11,13] and has also been structurally characterized. As a consequence of a non-resolvable disorder of the germanium atoms, a too short length of 2.213(1) Å was reported for the Ge−Ge double bond.[10] As a consequence of a better crystal quality, it has now been possible to resolve this disorder and demonstrate the presence of two independent molecules with bond lengths of 2.2894(6) and 2.2635(15) Å, typical of digermenes with this substitution pattern. A figure is not provided here because the forms of the two molecules do not differ from that already reported.[10]

Experimental Section

General Procedures. All manipulations were carried out in oven-dried glassware under an atmosphere of dry argon. The ^{1}H and ^{13}C NMR spectra were obtained on a Bruker ARX 500 spectrometer using C_6D_6 as solvent. The UV/vis spectra were recorded with a Comspec spectrometer with fiber optics. Elemental analyses were performed by Analytische Laboratorien, D-51779 Lindlar, Germany.

2,2,3,4,5,5-Hexakis(2,4,6-triisopropylphenyl)-1-selena-2,3,4,5-tetragermacyclopent-3-ene (3). Selenium (0.10 g, 12.7 mmol) and a few drops of Et_3P were added to a solution of **2** (0.62 g, 0.41 mmol) in *n*-hexane (30 mL), and the mixture was heated under reflux for 5 h. During this time the color changed from blue-black to yellow. *n*-Hexane was replaced by *n*-pentane (30 mL), excess selenium was filtered off, and the solvent was evaporated. Crystallization from a minimum amount of toluene provided yellow crystals of **3** (0.44 g, 67%): mp 118−120 °C; ^{1}H NMR δ 0.28 (d, 6 H, ^{3}J = 6.6 Hz), 0.47 (d, 6 H, ^{3}J = 6.6 Hz), 0.69 (d, 6 H, ^{3}J = 6.6 Hz), 0.74 (d, 6 H, ^{3}J = 6.6 Hz), 0.84 (d, 6 H, ^{3}J = 6.5 Hz), 0.88 (d, 6 H, ^{3}J = 6.5 Hz), 1.05 (d, 6 H, ^{3}J = 6.6 Hz), 1.12 (d, 6 H, ^{3}J = 6.5 Hz), 1.15 (d, 6 H, ^{3}J = 6.5 Hz), 1.18 (d, 6 H, ^{3}J = 6.6 Hz), 1.20 (d, 6 H, ^{3}J = 6.5 Hz), 1.22 (d, 6 H, ^{3}J = 6.5 Hz), 1.24 (d, 6 H, ^{3}J = 6.6 Hz), 1.30 (d, 6 H, ^{3}J = 6.6 Hz), 1.33 (d, 6 H, ^{3}J = 6.6 Hz), 1.35 (d, 6 H, ^{3}J = 6.6 Hz), 1.46 (d, 12 H, ^{3}J = 6.6 Hz), 2.68 (sept, 2 H), 2.72 (sept, 2 H), 2.82 (sept, 2 H), 3.20 (sept, 2 H), 3.26 (sept, 4 H), 3.58 (sept, 2 H), 3.94 (sept, 2 H), 6.96 (d, 2 H), 6.99 (d, 2 H), 7.03 (d, 2 H), 7.14 (d, 4 H), 7.25 (d, 2 H); ^{13}C NMR δ 14.20, 22.65, 23.75, 23.92, 24.08, 24.48, 24.64, 25.03, 25.24, 26.21, 26.47, 29.39, 30.16, 34.45, 34.55, 35.36, 36.87, 37.05, 121.72, 122.33, 122.58, 124.44, 141.12, 151.72, 154.01, 157.2; UV/vis (*n*-hexane) $\lambda_{max}(\epsilon)$ 399 nm (430). Anal. Calcd for $C_{90}H_{138}Ge_4Se$: C, 68.01; H, 8.75; Se, 4.97. Found: C, 67.65; H, 8.95; Se, 4.80. Single crystals of **3** were grown from toluene at −4 °C.

2,2,3,4,5,5-Hexakis(triisopropylphenyl)-1-oxa-2,3,4,5-tetragermacyclopentane (5). To a solution of **2** (0.40 g, 0.26 mmol) in *n*-hexane (30 mL) was added an excess of water (0.10 g, 5.5 mmol) and the mixture heated under reflux for 12 h. During this time the color changed from blue-black to pale orange. *n*-Hexane was replaced by *n*-pentane, and all insoluble products were filtered off. Crystallization from *n*-hexane at −4 °C furnished pale yellow crystals of **5** (0.33 g, 82%), mp 103−105 °C; ^{1}H NMR δ 0.47 (d, 6 H, ^{3}J = 6.6 Hz), 0.56 (d, 6 H, ^{3}J = 6.6 Hz), 0.61 (d, 6 H, ^{3}J = 6.6 Hz), 0.70 (d, 6 H, ^{3}J = 6.6 Hz), 0.74 (d, 6 H, ^{3}J = 6.6 Hz), 0.77 (d, 6 H, ^{3}J = 6.6 Hz), 0.99 (d, 6 H, ^{3}J = 6.6 Hz), 1.09 (d, 6 H, ^{3}J = 6.6 Hz), 1.16 (d, 6 H, ^{3}J = 6.6 Hz), 1.18 (d, 6 H, ^{3}J = 6.6 Hz), 1.20 (d, 6 H, ^{3}J = 6.6 Hz), 1.25 (d, 6 H, ^{3}J = 6.6 Hz), 1.29 (d, 6 H, ^{3}J = 6.6 Hz), 1.33 (d, 6 H, ^{3}J = 6.6 Hz), 1.36 (d, 6 H, ^{3}J = 6.6 Hz), 1.38 (d, 6 H, ^{3}J = 6.6 Hz), 1.41 (d, 6 H, ^{3}J = 6.6 Hz), 1.45 (d, 6 H, ^{3}J = 6.6 Hz), 2.67 (sept, 2 H), 2.72 (sept, 2 H), 2.82 (sept, 2 H), 3.20 (sept, 2 H), 3.26 (sept, 2 H), 3.60 (sept, 2 H), 3.70 (sept, 2 H), 4.02 (sept, 2 H), 4.20 (sept, 2 H), 5.61 (s, 2 H), 6.96 (d, 4 H), 6.99 (d, 2 H), 7.03 (d, 2 H), 7.18 (d, 2 H), 7.26 (d, 2 H); owing to the strongly twisted structure of **5**, all ^{1}H-resonances appear separately; ^{13}C NMR δ 23.75, 23.93, 23.98, 24.09, 24.21, 24.26, 24.48, 24.64, 25.03, 25.25, 26.22, 26.47, 29.39, 34.45, 35.36, 36.87, 37.05, 118.90, 121.60, 121.72, 122.30, 122.58, 122.77, 123.29, 123.76, 123.94, 124.44, 136.89, 139.84, 150.56, 150.97, 151.12, 151.72, 152.23, 154.01, 157.28, 159.69. Anal. Calcd for $C_{90}H_{140}Ge_4O$: C, 70.72; H, 9.23. Found: C, 70.45; H, 9.04. Single crystals of **5** were grown from toluene at −4 °C.

3,3,6,6-Tetrakis(2,4,6-triisopropylphenyl)-1,2,4,5-tetratellura-3,6-digermacyclohexane (6). Triethylphosphane telluride (0.30 g, 1.22 mmol, excess) was added to a solution of **2** (0.82 g, 0.54 mmol) in toluene (30 mL) and the mixture heated for 12 h at 80 °C. Toluene was replaced by *n*-pentane, and all insoluble compounds were filtered off. The solvent was evaporated and the residue redissolved in toluene to afford a small amount of dark red crystals of **7**. Crystallization from methylcyclopentane furnished a small amount of yellow crystals of **8**. Repeated crystallization from *n*-hexane yielded pale red crystals of **6** (0.12 g, 15% yield), mp > 210 °C (dec); ^{1}H NMR δ 0.88 (d, 12 H, ^{3}J = 6.6 Hz), 0.95 (d, 6 H, ^{3}J = 6.7 Hz), 1.00 (d, 6 H, ^{3}J = 6.6 Hz), 1.12 (d, 24 H, ^{3}J = 6.6 Hz), 1.17−1.46 (m, 24 H), 2.67 (sept, 4 H), 3.37 (sept, 4 H), 4.53 (sept, 4 H), 6.99 (s, 4 H), 7.08 (s, 4 H); ^{13}C NMR δ 22.33, 22.59, 22.99, 23.57, 23.94, 24.57, 27.09, 31.90, 34.51, 35.48, 37.82, 122.71, 124.65, 129.34, 136.77, 143.07, 150.80, 151.51, 153.22. Anal. Calcd for $C_{60}H_{92}Ge_2Te_4$: C, 49.06; H, 6.31. Found: C, 50,69; H, 6.70. Single crystals of **6** were grown from *n*-hexane at −4 °C.

2-Methoxy-*N*-[1,1,2,3-tetrakis(2,4,6-triisopropylphenyl)-4(1*H*)-trigermethylidene]aniline (9). To a solution of **2** (0.44 g, 0.29 mmol) in *n*-hexane (30 mL) was added 0.5 mL of 2-methoxyphenyl isocyanide (0.54 g, 4.1 mmol), and the mixture was heated for 3 h at 60 °C. During this time the color

---

(10) Schäfer, H.; Saak, W.; Weidenbruch, M. *Organometallics* **1999**, *18*, 3159.

(11) Park, J.; Batcheller, S. A., Masamune, S. *J. Organomet. Chem.* **1989**, *367*, 39.

(12) Lee, V. Y.; Ichinohe, M.; Sekiguchi, A. *J. Am. Chem.* Soc. **2000**, *122*, 12604.

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

Table 1. Crystallographic Data for 3, 5, 6, and 7

	3	**5**	**6**	**7**
formula	$C_{90}H_{138}Ge_4Se\cdot 1.5\ C_7H_8$	$C_{90}H_{140}Ge_4O\cdot {}^1/_2C_7H_8$	$C_{60}H_{92}Te_4\cdot {}^1/_2C_6H_{14}$	$C_{60}H_{92}Ge_4Te_6\cdot 4C_7H_8$
fw	1589.46	1528.51	1468.99	1869.41
a (Å)	14.9502(7)	15.0722(4)	10.5768(3)	17.5800(6)
b (Å)	17.0382(11)	15.0795(5)	15.9415(7)	28.5040(14)
c (Å)	20.5480(9)	23.4233(10)	21.3704(9)	18.3953(8)
α (deg)	69.423(6)	98.857(5)	80.087(5)	90
β (deg)	79.093(5)	99.257(4)	82.569(5)	90
γ (deg)	85.579(7)	117.922(3)	85.286(3)	90
V (Å^3)	4811.3(4)	4479.3(3)	3513.0(2)	9217.9(7)
Z	2	2	2	4
D_{calcd} (g cm^{-3})	1.192	1.166	2.516	1.613
cryst size (mm)	0.80 × 0.30 × 0.14	0.47 × 0.24 × 0.16	0.50 × 0.19 × 0.02	0.20 ×0.13 × 0.04
cryst syst	triclinic	triclinic	triclinic	orthorhombic
space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	*Pbca*
$2\theta_{max}$ (deg)	52	52	52	52
no. of reflns measd	58 725	41 366	43 491	64 739
no. of unique reflns	17 308	16 428	12 802	8852
R ($I > 2\sigma(I)$)	0.0415	0.0395	0.0298	0.0407
wR_2 (all data)	0.1068	0.1012	0.0693	0.0762
GOF (F^2)	0.930	0.971	0.909	0.741

changed from blue-black to red. *n*-Hexane was replaced by *n*-pentane, and all insoluble products were filtered off. *n*-Pentane was evaporated and the residue redissolved in *n*-hexane to furnish dark red crystals of **9** (0.20 g, 59%), mp 87−89 °C; ^{1}H NMR δ 0.69 (d, 6 H, $^3J = 6.6$ Hz), 0.74 (d, 6 H, $^3J = 6.6$ Hz), 1.06 (d, 6 H, $^3J = 6.6$ Hz), 1.13 (d, 6 H, $^3J = 6.6$ Hz), 1.17 (d, 6 H, $^3J = 6.6$ Hz), 1.19 (d, 6 H, $^3J = 6.6$ Hz), 1.21 (d, 6 H, $^3J = 6.6$ Hz), 1.26 (d, 6 H, $^3J = 6.6$ Hz), 1.29 (d, 6 H, $^3J = 6.6$ Hz), 1.33 (d, 6 H, $^3J = 6.6$ Hz), 1.35 (d, 6 H, $^3J = 6.6$ Hz), 1.46 (d, 6 H, $^3J = 6.6$ Hz), 2.67−2.82 (m, 12 H), 3.31 (s, 3 H), 6.30−6.45 (m, 4 H), 6.88 (d, 2 H), 6.98 (d, 2 H), 7.11−7.15 (m, 4 H); ^{13}C NMR δ 24.07, 24.18, 24.38, 24.86, 34.62, 34.72, 35.99, 38.87, 55.71, 112.34, 118.52, 120.35, 121.18, 121.86, 122.16, 122.37, 125.20, 140.45, 144.37, 146.27, 149.52, 150.49, 151.14, 151.98, 153.20, 153.78; UV/vis (*n*-hexane) $\lambda_{max}(\epsilon)$ 406 nm (43400, tailing off in the red region). Anal. Calcd for $C_{68}H_{99}Ge_3NO$: C, 70.14; H, 8.57. Found: C, 69.81; H, 8.70. Single crystals of **9** were grown from methylcyclopentane at −4 °C. Crystallization from diethyl ether furnished the already known tetrakis(2,4,6-triisopropylphenyl)digermene (**10**).

Crystallographic Analyses. Crystal and numerical data of the structure determinations are given in Table 1 and Table 2. In each case the crystal was mounted in an inert oil. Data collection was performed with a Stoe IPDS area detector at 193(2) K using graphite-monochromated Mo Kα radiation. The structures were solved by direct phase determination and refined by full-matrix least-squares techniques against F^2 with the SHELXL-97 program system.[14] Hydrogen atoms were placed in the calculated positions, and all other atoms were refined anisotropically. The data have been deposited with the Cambridge Crystallographic Data Centre: CCDC-216 885 (**3**), CCDC-216 888(**5**), CCDC-216 883 (**6**), CCDC-216 890 (**7**), CCDC-216 887 (**8**), CCDC-216 886 (**9**), and CCDC-216 889 (**10**).

Table 2. Crystallographic Data for 8, 9, and 10

	8	**9**	**10**
formula	$C_{60}H_{92}Ge_2Te$	$C_{68}H_{99}Ge_3NO\cdot 2C_6H_{12}$	$C_{60}H_{92}Ge_2$
fw	1090.15	1164.35	958.52
a (Å)	22.4018(5)	11.8412(2)	13.1667(6)
b (Å)	9.7280(3)	32.2192(11)	13.5646(7)
c (Å)	26.7946(5)	21.0546(6)	18.2962(7)
α (deg)	90	90	98.402(5)
β (deg)	96.545(3)	101.127(3)	96.913(5)
γ (deg)	90	90	112.121(5)
V (Å^3)	5801.1(3)	7881.6(4)	2939.2(2)
Z	4	4	2
D_{calcd} (g cm^{-3})	1.248	1.123	1.083
cryst size (mm)	0.33 × 0.23 × 0.15	0.70 × 0.05 × 0.05	0.30 × 0.23 × 0.10
cryst syst	monoclinic	monoclinc	triclinic
space group	$C2/c$	$P2_1/n$	$P\bar{1}$
$2\theta_{max}$ (deg)	52	52	52
no. of reflns measd	22 519	65 598	36 591
no. of unique reflns	5403	14 553	10 752
R ($I > 2\sigma(I)$)	0.0336	0.0557	0.0346
wR_2 (all data)	0.0895	0.1272	0.0706
GOF (F^2)	1.015	0.848	0.847

Acknowledgment. Financial support of our work by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie is gratefully acknowledged.

Supporting Information Available: Listing of atomic coordinates, anisotropic displacement parameters, and bond lengths and angles for **3**, **5**, **6**, **7**, **8**, **9**, and **10**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM034123E

---

[14] Sheldrick, G. M. *SHELXL-97*, Program for crystal structure refinement; Universität Göttingen: Göttingen, Germany, 1997.