Registry No. 6, 118630-65-2; **7**, 118630-66-3; **8**, 118655-60-0; **10**, 50684-40-7; **11**, 118655-61-1; **12**, 118630-67-4; **13** (R = Ph), 118630-68-5; **13** (R = H), 118630-69-6; **15** (R = Ph), 118630-70-9; **15** (R = H), 118630-71-0; **16**, 118630-72-1; **17**, 65038-76-8; **18**, 118655-62-2; **19**, 118630-73-2; **20**, 118630-74-3; **21**, 118630-75-4; Bu_3SnH, 688-73-3.

Oxygenation of Digermene Derivatives

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We report herein that tetrakis(2,6-diethylphenyl)digermene (**1**)[1] and tetrakis(2,6-diisopropylphenyl)digermene (**1a**)[2] undergo oxygenation through several discrete pathways to provide the corresponding 1,2-digermadioxetane (**2**, **2a**), 1,3-cyclodigermoxane (**3**, **3a**), and digermoxirane (**4**, **4a**) derivatives, as shown in Scheme I. These derivatives represent three hitherto unknown ring systems, and the crystal structures of **2** and **3** are disclosed. Scheme I is analogous in several ways to that for oxygenation pathways of disilene derivatives,[3] but significant differences are also noted between the germanium and silicon series.

Exposure of **1** in toluene to dioxygen at −78 °C or 20 °C provided **2**[4] quantitatively, which upon heating at 90 °C was isomerized to **5** (see below for its structural determination). Photolysis of **2** took an entirely different course to afford **3**. The thermal and photochemical behavior of **2** contrasts with that of **6**, one of the low-temperature (−78 °C) oxygenation products of the stable disilene RR′Si=SiRR′ (R = mesityl, R′ = *tert*-butyl).[3a] Compound **6**[5] undergoes *thermal* rearrangement at 0 °C or above to provide **7** quantitatively. The crystal structure of **3** is compared below with that of **7** which has demonstrated a unique structural feature.[3a,b]

Compound **3** was also obtained directly and quantitatively from **1** with an excess of dimethyl sulfoxide or *N*-methylmorpholine-*N*-oxide in toluene at room temperature. Treatment of **1** with nitrous oxide effected a [2 + 3] addition to provide **4** upon loss of N_2. Since conversion of **4** into **3** with DMSO proceeded very rapidly as compared with that of **1** into **3** effected by the same reagent, **4** appears to be a likely intermediate in this latter conversion.

The majority of the above oxygenation experiments with **1** have been duplicated with **1a** as shown in Scheme I. An exception was conversion of **1a** to **3a** which was too slow to be observed.

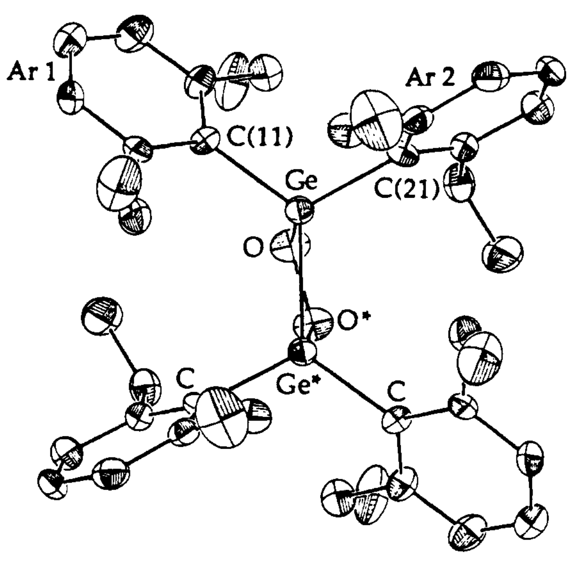
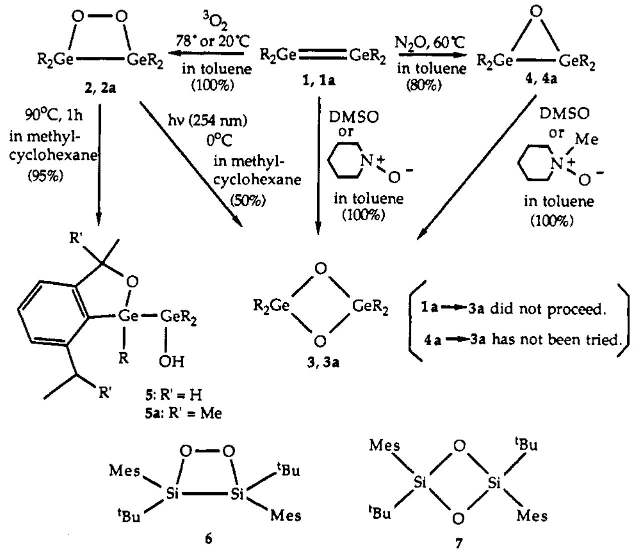


Figure 1. ORTEP diagram of **2**. Selected bond distances and angles are as follows: Ge–Ge* 2.441 (2) Å; O–O* 1.47 (1) Å; O–Ge = O*–Ge* 1.857 (5) Å; Ge–C(11) 1.958 (6) Å; Ge–C(21) 1.970 (7) Å; O–Ge–Ge* 74.1 (1)°; O*–O–Ge 103.9 (2)°; O–Ge–C(11) 102.8 (2)°; O–Ge–C(21) 115.0 (3)°.

Scheme I. Oxygenation of **1** and **1a**[a]



[a] R = 2,6-diethylphenyl for **1–5** and R = 2,6-diisopropylphenyl for **1a–5a**. The yields indicated are those for the **1** series.

Compound **5a**, the thermolysis product of **2a**, has been crystallographically identified as shown,[6] and by analogy the corresponding structure is assigned to **5** (see above).

Crystallographic Analysis of 2.[4,7] Compound **2** crystallizes as a discrete molecular unit with space group imposed 2-fold symmetry, and the C_2 axis bisects both the Ge–Ge and O–O bonds. Selected bond lengths and angles are shown in Figure 1. The central Ge_2O_2 trapezoidal core deviates significantly from planarity as is evident from the Ge–O–O*–Ge* torsion angle of 19.5°. The Ge–Ge* bond length is slightly shorter than normal Ge–Ge bond

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[1] (a) Snow, J. T.; Murakami, S.; Masamune, S.; Williams, D. J. *Tetrahedron Lett.* **1984**, *25*, 4191. (b) Also, see: Masamune, S.; Hanzawa, Y.; Williams, D. J. *J. Am. Chem. Soc.* **1982**, *104*, 6136. (c) Batcheller, S. A.; Masamune, S. *Tetrahedron Lett.* **1988**, *29*, 3383. (d) Ando, W.; Tsumuraya, T. *Ibid.* **1986**, *27*, 3251. (e) For a review, see: Masamune, S. In *Silicon Chemistry*, Corey, E. R., Corey, J. Y., Gaspar, P. P. Eds.; Ellis Horwood Ltd.: New York, 1988; Chapter 25.

[2] The synthesis of **1a** will be published elsewhere.

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[4] The physical properties of new compounds and further information on the X-ray crystal analyses of **2** and **3** are detailed in the Supplementary Material.

[5] The structural assignment of **6** as shown in Scheme I was based on its spectral data but not by crystallography. The authors (ref 3a) were cautious and are probably correct in choosing between the 1,2-disiladioxetane and disilaethylene perepoxide structures.

[6] Full information on the crystal structure of compound **5a** is available from S.M. upon request.

[7] Compound **2**: $C_{40}H_{52}O_2Ge_2$, M = 710.0 g/mol, monoclinic, a = 18.883 (8) Å, b = 9.442 (4) Å, c = 21.335 (9) Å, β = 111.49 (2)°, V = 3539 (4) Å^3, Z = 4, space group $I2/a$, D_{calcd} = 1.33 g cm^{-1}. Data were collected at −65 °C with Mo Kα radiation (graphite monochromator λ = 0.71069 Å) on an Enraf-Nonius CAD-4. Total of 4482 reflections measured ($+h,+k\pm l$: 3° $\leq 2\theta \leq$ 55°), 4371 unique, R_{int} = 0.057. Data corrected for Lorentz polarization and absorption effects (transmission coefficients 0.73–1.08). Structure solved by direct methods.[8] Convergence on 2057 reflections [$I > 3.0\sigma(I)$] and 208 parameters resulted in R = 0.059 and R_w = 0.062 (p = 0.03).

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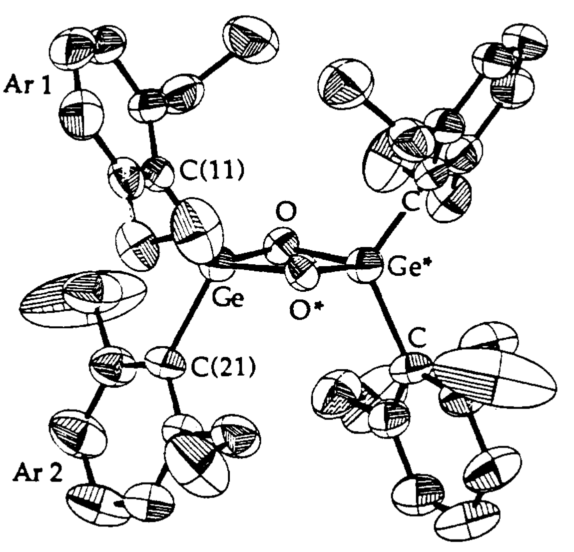

Figure 2. ORTEP diagram of **3**. Selected bond distances and angles are ass follows: Ge–O = Ge*–O* 1.820 (2) Å; Ge–O* = Ge*–O 1.814 (2) Å; Ge–Ar 1.951 Å and 1.956 Å; Ge–O–Ge* = Ge–O*–Ge 92.1 (1)°; O–Ge–O* = O–Ge*–O* 87.6 (1)°. Ge,Ge* distance 2.617 (1) Å.

lengths (2.46 Å),[9] while the Ge–O bond length is somewhat longer than others recorded (1.77 Å).[9] These deviations may be due to the constraint in forming the strained ring system. All of the four bulky 2,6-diethylphenyl groups lie below the Ge–Ge* side of the trapezoidal core. The lone pair–lone pair repulsion of the dioxetane oxygens and possibly minimization of the steric congestion of the aryl groups may lead to puckering of the four-membered ring. The aryl groups occupy a roughly helical arrangement about each germanium atom: the dihedral angles between the aryl planes and the C(11)–Ge–C(21) plane are 65.5° (for aryl group 1) and 61.2° (for aryl group 2).

Crystallographic Analysis of 3.[4,10] The crystal structure of **3** possesses a crystallographic 2-fold axis bisecting an approximately square but slightly puckered cyclodigermoxane ring with Ge–O distances and angles shown in Figure 2.[9] The dihedral angles between the two Ge–Ge*–O planes and between the two O–Ge–O* planes are 8.8 (2)° and 8.4 (1)°, respectively. The C(11)–Ge–C(21) plane is roughly orthogonal to the cyclodigermoxane ring with a slight twist angle of 9.5 (1)° along the Ge–Ge* axis. The aryl rings are attached to the cyclogermoxane ring in a roughly helical fashion and intersect the C–Ge–C plane with dihedral angles of 60.8° (for aryl 1) and 63.9° (for aryl 2).

A brief comment appears appropriate on the crystal structure of **3** in comparison with the silicon analogue **7** and other cyclodisiloxanes which were found earlier to possess silicon, silicon *distances* which are normal for, or even shorter than, a Si–Si *bond* length (2.34–2.35 Å).[3b] Both the cyclodigermoxane and cyclodisiloxane rings are nearly square. In the former (**3**) the Ge–O bond length (1.857 Å) is long enough to accommodate the two germanium atoms with a Ge,Ge distance of 2.617 (1) Å, well beyond a Ge–Ge normal bond length (2.46 Å), leading to the straightforward formulation that the cyclodigermoxane ring is constructed with four equivalent localized Ge–O bonds. In contrast, the Si–O bonds (1.66–1.68 Å), comparatively shorter than Ge–O, may in effect be "squeezing" the two silicon atoms together to minimize internal strains elsewhere in the molecule including the O,O repulsion. It is interesting to note that a normal Si–Si bond length is not significantly different from a Ge–Ge length.

Supplementary Material Available: Listings of atom coordinates and temperature factors, bond lengths, bond angles, and anisotrophic temperature factors of compounds **2** and **3** as well as physical properties (mp, UV, ^{1}H NMR) of new compounds (26 pages). Ordering information is given on any current masthead page.

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(9) (a) Ross, L.; Dräger, M. *J. Organomet. Chem.* **1980**, *199*, 195. (b) Dräger, M.; Ross, L. Z. *Anorg. Allg. Chem.* **1981**, *476*, 95. (c) Jensen, W.; Jacobson, R. *Cryst. Struct. Commun.* **1975**, *4*, 299. (d) Glidewell, C.; Liles, D. C. *Acta Crystallogr.* **1978**, *B34*, 119. (e) Glidewell, C.; Rankin, W. H.; Robiette, A. G.; Sheldrick, G. M.; Beagley, B.; Cradock, S. *J. Chem. Soc. A* **1970**, 315.

(10) Compound **3**: $C_{40}H_{52}Ge_2O_2$, M = 710.0 g/mol, orthorhombic, a = 19.362 (7) Å, b = 19.454 (5) Å, c = 9.638 (1) Å, V = 3630 (3), space group *Pnab* $Z = 4$, D_{calcd} = 1.30 g cm^{-1}. Data were collected at room temperature by using Cu Kα radiation (graphite monochromator λ = 1.5405 Å) on a Rigaku AFC-5 diffractometer: 2627 unique, observed [$F > 3\sigma(F)$] with $2\theta \leq 126°$. Data were corrected for Lorentz polarization effects but not for absorption. Structure solved by direct methods.[11] Convergence at R = 0.068 and R_w = 0.1060 (p = 0.01).

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A New Mode of Carbene Reactivity: Coupling with Two Alkynes To Generate Highly Substituted Cyclopentadiene Products

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The metal-mediated coupling of two alkynes with a carbene to generate five-membered carbocycles has not previously been realized, in part due to competitive reactions such as alkyne polymerization[1] or CO incorporation into the cyclized products.[2] A potential method for circumventing these competitive reactions is to introduce the carbene moiety at the metal center subsequent to alkyne complexation. Our approach to this problem therefore involves the intermediacy of a metallacycle, generated from two alkynes, which is then converted to a carbocycle, possibly via a metallacycle–carbene species.[3] An advantage of this route lies in the large number of metal complexes which readily form metallacycles upon reaction with alkynes and the observation that these metallacycles often react with a variety of cycloaddends to form carbocycles or heterocycles.[4] Employment of a carbene cycloaddend, in contrast to CO,[4c] would allow for direct introduction of an sp^3 carbon center into the five-membered ring product. Herein we report the successful metal-mediated cyclization of two different alkynes and a carbene to generate substituted η^4-cyclopentadiene cobalt products, with a high degree of regio- and stereoselectivity.

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