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Cyclotrigermenes: A New Unsaturated Ring System

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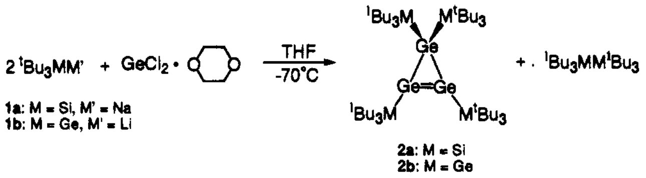
Over the past decade, dramatic progress has been made in the chemistry of dimetallenes and cyclotrimetallanes composed of the group 14 elements heavier than carbon.[1] The use of steric and electronic stabilization allowed the isolation of $R_2M{=}MR_2$ and $(R_2M)_3$ (M = Si, Ge, and Sn).[1,2] Nevertheless, up to now the isolation and characterization of the unsaturated three-membered cyclotrimetallene, which is of interest in itself and also as a possible precursor of triply bonded dimetallyne ($RM{\equiv}MR$), has never been reported.

We report herein the first successful synthesis of cyclotrigermenes tetrakis(tri-*tert*-butylsilyl)cyclotrigermene (**2a**) and tetrakis(tri-*tert*-butylgermyl)cyclotrigermene (**2b**) together with ab inito calculations of H_3Si- and H_3Ge-substituted cyclotrigermenes. Cyclotrigermenes **2a** and **2b** were synthesized by the reactions of $GeCl_2$–dioxane with *t*-Bu_3SiNa and *t*-Bu_3GeLi in THF, respectively (Scheme 1).

For the synthesis of **2a**, a suspension of 1.36 g of $GeCl_2$–dioxane (5.87 mmol) in THF (20 mL) was cooled to −70 °C, and 2 equiv of *t*-Bu_3SiNa (**1a**)[3] in THF (30 mL) was added over a period of 10 min and stirred overnight. After removal of the resulting salt, the filtrate was condensed in vacuo. The reaction mixture contained **2a**, hexa-*tert*-butyldisilane, and tri-*tert*-butylsilane. Crystallization from heptane gave the crude **2a**, which was purified by gel permeation chromatography equipped with a recycling system by using toluene to afford dark red crystals of **2a** (397 mg, 20%).

Scheme 1



For the synthesis of **2b**, a solution of *t*-Bu_3GeLi (**1b**) was prepared by the reaction of *t*-Bu_3GeCl (3.08 g, 11.0 mmol) with Li (0.3 g, 43.2 mmol) in THF (30 mL). A suspension of 1.23 g of $GeCl_2$–dioxane (5.31 mmol) in THF (10 mL) was cooled to −70 °C, and 2 equiv of *t*-Bu_3GeLi was added over a period of 10 min and stirred overnight. After removal of the resulting salt, the filtrate was condensed. The residue was chromatographed on silica gel with hexane under argon followed by further purification by gel permeation chromatography to afford dark red crystals of **2b** (280 mg, 13%).

The reaction mechanism to produce cyclotrigermenes **2a** and **2b** is not clear at this moment; however, the use of bulky silyl and germyl anions is crucial. Otherwise, only substitution reactions occur to form germylene.[4,5] The choice of *t*-Bu_3Si or *t*-Bu_3Ge is very important for the successful synthesis of the cyclotrigermenes. Theoretical calculation indicates that electropositive substituents such as silyl and germyl groups lead to a remarkable relief of the strain of three-membered rings comprising the group 14 elements.[6,7]

The NMR spectra of **2a** and **2b** are very simple in accordance with their symmetrical structures.[8] Owing to decomposition in matrix solvents, the FAB mass spectra could not be obtained. The DEI mass spectrum of **2a** showed no molecular ion peaks, but the relatively intense peaks, attributable to the tris(tri-*tert*-butylsilyl)cyclotrigermenyl cation by loss of the tri-*tert*-butylsilyl group, appeared in the mass range 809–824 in agreement with the formula of $C_{36}H_{81}Si_3Ge_3$.

The structures of **2a** and **2b** were confirmed by X-ray crystallography, but precise structural data could not be obtained due to the significant disorder of the *tert*-butyl groups. However, the positions of the skeleton were determined with sufficient accuracy to discuss its structural features, showing that the cyclotrigermenes **2a** and **2b** have completely trigonal-planar geometries with $Ge{=}Ge$ distances of 2.239(4) Å (Figure 1).[9]

The structures were successfully reproduced by theoretical calculations of H_3Si-substituted cyclotrigermene (**2c**) and H_3-

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(5) In contrast to our results, the reaction of $(Me_3Si)_3SiLi(thf)_3$ with $GeCl_2$–dioxane is reported to produce the unexpected disilagermirane. See ref 2q.

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(8) Spectral data, **2a**: dark red crystals; mp 157 °C dec; ^1H NMR (C_6D_6, δ) 1.39 (s, 54 H), 1.52 (s, 54 H); ^{13}C NMR (C_6D_6, δ) 26.1 ($C(CH_3)_3$), 28.7 ($C(CH_3)_3$), 32.3 ($C(CH_3)_3$), 34.6 ($C(CH_3)_3$); ^{29}Si NMR (C_6D_6, δ) 37.2, 50.1; UV (λ_{max}, ϵ) 217 (94 000), 311 (21 000). Anal. Calcd for $C_{48}H_{108}Si_4Ge_3$: C, 56.77; H, 10.72. Found: C, 56.71; H, 10.61. **2b**: dark red crystals; mp 178 °C dec; ^1H NMR (C_6D_6, δ) 1.45 (s, 54 H), 1.57 (s, 54 H); ^{13}C NMR (C_6D_6, δ) 32.5 ($C(CH_3)_3$), 33.8 ($C(CH_3)_3$), 34.7 ($C(CH_3)_3$), 36.4 ($C(CH_3)_3$); UV (λ_{max}, ϵ) 221 (55 000), 326 (13 000). Anal. Calcd for $C_{48}H_{108}Ge_7$: C, 48.30; H, 9.12. Found: C, 48.57; H, 9.02.

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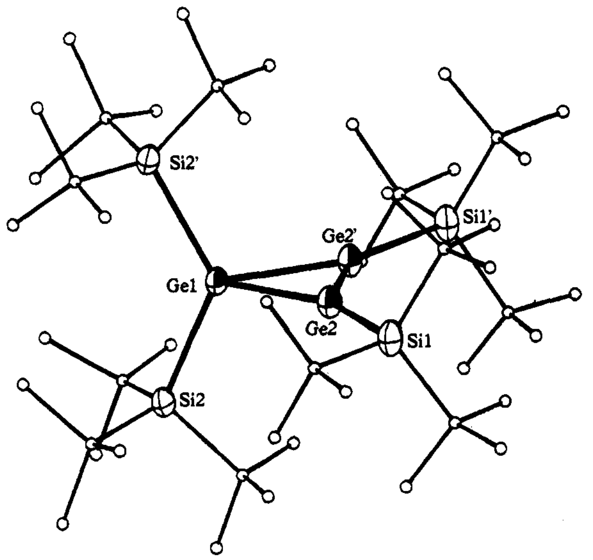

Figure 1. ORTEP diagram (30% probability ellipsoids for Ge and Si) for **2a**. Selected bond lengths (Å): Ge1−Ge2 2.522(4), Ge2−Ge2′ 2.239(4), Ge1−Si2 2.629(7), Ge2−Si1 2.448(7). Selected bond angles (deg): Ge2−Ge1−Ge2′ 52.7(1), Ge1−Ge2−Ge2′ 63.6(1), Si2−Ge1−Si2′ 129.8(2), Ge1−Ge2-Si1 152.7(2), Ge2′−Ge2−Si1 143.6(2).

Ge-substituted cyclotrigermene (**2d**) at the HF/DZ+d level (Figure 2).[10] The optimized structures with a planar Ge=Ge double bond correspond to a minimum with Ge=Ge double bond distances of 2.228 Å (**2c**) and 2.231 Å (**2d**). The structures of digermenes have been much studied experimentally and theoretically.[11] In contrast to cyclotrigermenes, the digermenes reported so far have *trans*-bent structures with folding angles of 12−36° and Ge=Ge distances of 2.213−2.347 Å.[11a−d]

Owing to the large steric congestion, no addition reaction occurred with ethanol or diazomethane at room temperature. However, the cyclotrigermenes readily decompose with oxidants like tetracyanoethylene and tris(*p*-bromophenyl)aminium hexachloroantimonate.

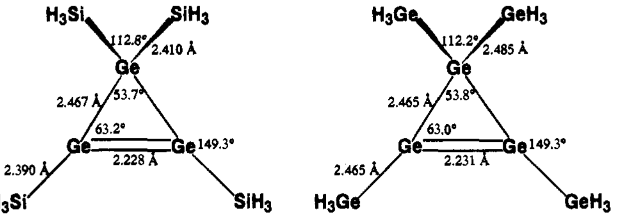

Figure 2. The optimized geometries for **2c** and **2d** (HF/DZ+d).

The cyclotrigermenes are thermally labile and photosensitive. On heating at 100 °C in toluene, they decompose with change of color to give tri-*tert*-butylsilane and hexa-*tert*-butyldisilane for **2a**, tri-*tert*-butylgermane and hexa-*tert*-butyldigermane for **2b**, arising from cleavage of the exocyclic Ge−Si or Ge−Ge bonds. Irradiation with light of greater than 300 nm wavelength gave the same results. However, no evidence for cycloelimination to produce a triply bonded digermyne and germylene was obtained.

Experiments concerning the synthesis of other cyclotrimetallenes consisting of Si and Sn are in progress.

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Supporting Information Available: Details of X-ray experiments on **2a**,**b** (12 pages); observed and calculated structure factors for **2a**,**b** (29 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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(9) During X-ray diffraction, a single crystal of **2a** in a capillary glass decomposed within 1 day due to its instability. A single crystal of **2b** had the same trouble. Crystal data of **2a**: MF = $C_{48}H_{108}Si_4Ge_3$, MW = 1015.6, orthorhombic, a = 21. 796(5) Å, b = 12.792(4) Å, c = 23.995(8) Å, V = 6690(6) Å^3, space group *Cmcm*, Z = 4, D_{calcd} = 1.008 g/cm^3, R = 0.122. Crystal data of **2b**: MF = $C_{48}H_{108}Ge_7$, MW = 1193.5, orthorhombic, a = 21. 864(5) Å, b = 12.882(2) Å, c = 24.194(3) Å, V = 6814(4) Å^3, space group *Cmcm*, Z = 4, D_{calcd} = 1.163 g/cm^3, R = 0.101. For **2b**, Ge(2)−Ge2′ 2.239(5) Å and Ge1−Ge2 2.505(6) Å, Ge2−Ge1−Ge2′ 53.1(1)° and Ge1−Ge2−Ge2′ 63.5(1)°. The crystals were exchanged several times in all crystals, but the refinements were not improved. Low-temperature (150 K) data collection was also unsuccessful.

(10) The calculations were carried out using the Gaussian 92/DFT program with the DZ basis sets and effective core potentials on Si and Ge (Wadt, W. R.; Hay, P. J. *J. Chem. Phys.* **1985**, *82*, 284), DZ being augmented by a set of five d-type polarization functions (d exponents 0.45 (Si) and 0.246 (Ge)).

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