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The First Halogen-Substituted Cyclotrigermenes: A Unique Halogen Walk over the Three-Membered Ring Skeleton and Facial Stereoselectivity in the Diels−Alder Reaction

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The chemistry of unsaturated three-membered ring compounds consisting of heavier group 14 elements, cyclotrimetallenes, has attracted considerable attention because of their unique structures and has developed very rapidly.[1−7] In 1995, we reported the first synthesis of cyclotrigermene (R_4Ge_3, R = $^tBu_3Si$ and $^tBu_3Ge$) constituting an unsaturated three-membered skeleton.[2a] We have subsequently succeeded in transforming cyclotrigermene to cyclotrigermenylium ion ($R_3Ge_3^+$),[2b,c,e] which has been a long-sought free germyl cation with a 2π-electron system. Very recently, we have also shown the reaction of the cyclotrigermenylium ion with appropriate bulky nucleophiles to produce the corresponding unsymmetrically substituted cyclotrigermenes,[2d] which opens a new synthetic route for cyclotrimetallenes.

However, the heteroatom-substituted cyclotrimetallenes are completely unknown, due to synthetic difficulties and their instability. It is quite interesting to introduce electronegative substituents, particularly a halogen (X) atom, at the saturated position of the skeleton. This would produce not only changes in the geometry of the three-membered skeleton but also significant effects on the reactivity, arising from the interaction between the low-lying σ^*-orbital of the exo Ge−X bond and a high-lying π-orbital of the endocyclic Ge═Ge double bond. Herein, we report the synthesis, structure, and the unique dynamic behavior of halogen-substituted cyclotrigermenes, as well as facial selectivity in the Diels−Alder reaction with butadiene.

Air-sensitive dark red crystals of the halogen-substituted cyclotrigermenes **2a**−**2c** were obtained by the reaction of $[(^tBu_3Si)_3Ge_3]^+\cdot$TTFPB$^-$ ($\mathbf{1}^+\cdot$TTFPB$^-$; TTFPB$^-$ = tetrakis(2,3,5,6-tetrafluorophenyl)borate) with potassium halides (KCl, KBr, or KI) in oxygen-free dry diethyl ether at room temperature in 60−74% yields (Scheme 1).[8]

X-ray crystallographic analyses of **2a**−**2c** established the exact structure.[9] In all of the halogen-substituted cyclotrigermenes, the three-membered ring represents an almost-isosceles triangle; for example, **2b** has bond angles of 56.07(2), 61.95(3), and 61.99(3)°. The Ge═Ge double bond length of **2b** is 2.2743(8) Å, being lengthened relative to that of tetrakis(tri-*tert*-butylsilyl)cyclotrigermene (**3**) (2.239(4) Å),[2a] whereas the Ge−Ge single bonds (2.4191(9) and 2.4200(9) Å) are shortened compared with those of **3** (2.522(4) Å). Similar structural changes of the unsaturated three-membered skeleton can be seen in **2a** and **2c**.[10] The geometry around the Ge═Ge double bond is *trans*-bent in **2a** but highly *cis*-bent in **2b** and **2c**, as determined by the folding angles (**2b**: 45.1 and 10.2° **2c**: 43.3 and 8.0°) (Figure 1).

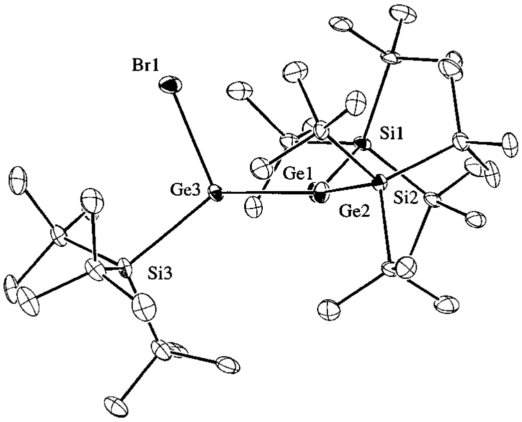
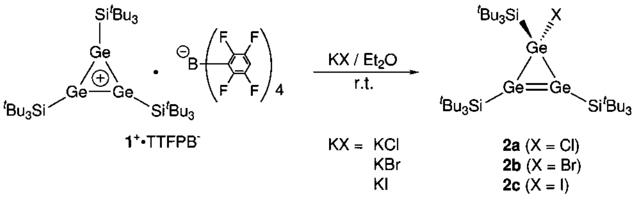


Figure 1. ORTEP drawing of **2b** (side view). Hydrogen atoms are omitted for clarity. Selected bond lengths (Å): Ge1−Ge2 2.2743(8), Ge1−Ge3 2.4191(9), Ge2−Ge3 2.4200(9), Ge3−Br1 2.4253(10). Selected bond angles (deg): Ge2−Ge1−Ge3 61.99(3), Ge1−Ge2−Ge3 61.95(3), Ge1−Ge3−Ge2 56.07(2). Selected torsion angles (deg): Si1−Ge1−Ge2−Ge3 134.90(9), Si2−Ge2−Ge1−Ge3 −169.83(12).

Scheme 1



The introduction of an electronegative group, such as a halogen atom, at the endocyclic sp^3 germanium atom results in the lengthening of the Ge═Ge double bond and the shortening of the Ge−Ge single bond. These changes in bond length can be explained by the σ^*-aromaticity concept,[11] that is, the interaction between the σ^*-orbital of the Ge−X bond and the Ge═Ge π-orbital. This σ^*−π interaction also leads to the remarkable *cis*-bent geometry around the Ge═Ge double bond, as found in **2b** and **2c**. The *cis*-bent Ge═Ge double bonds in **2b** and **2c** are well reproduced by density functional calculations of the model compound $Ge_3(SiH_3)_3X$ (X = Br, I) and real molecules $Ge_3(Si^tBu_3)_3X$ (X = Br, I) at the B3LYP/DZd level.[12] No energy minimum was found for the *trans*-bent form, suggesting that the *cis*-bent geometry in **2b** and **2c** is due to the electronic effect.[13]

These structural features of the halogen-substituted cyclotrigermenes bring about unique dynamic behavior in solution. At room temperature, the ^{1}H NMR spectrum of **2b** in toluene-d_8 gave one sharp signal at 1.38 ppm, and no peaks were observed in the ^{29}Si NMR spectrum. However, the ^{1}H NMR signal was broadened on lowering the temperature and split into two peaks at 1.29 and

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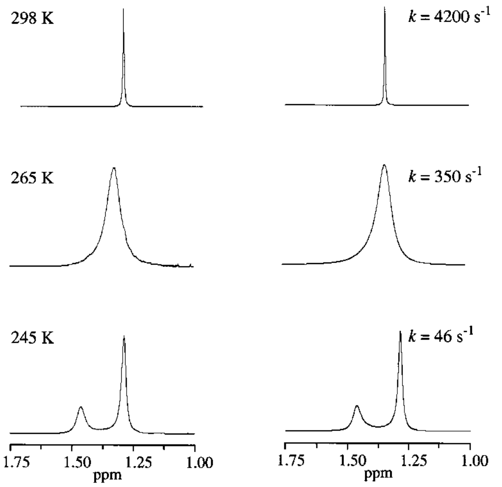
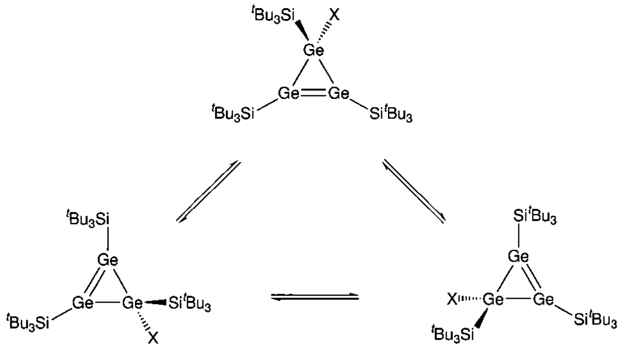


Figure 2. Temperature-dependent ^1H NMR spectra of **2b** in toluene-d_8: observed (left) and simulated (right).

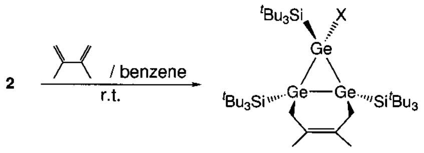
Scheme 2



1.45 ppm with 2:1 intensity ratio below 250 K. In the ^{29}Si NMR spectrum at 210 K, two signals were observed at 44.7 and 27.1 ppm in the ratio of 2:1. These spectral changes indicate that bromine migration occurs on the NMR time scale. The activation parameters for Br migration in **2b** were estimated by temperature-dependent ^1H NMR spectra, measuring from 245 to 298 K ($E_a = 53.8$ kJ·mol^{-1}, $\Delta H^\ddagger = 51.6$ kJ·mol^{-1}, $\Delta S^\ddagger = -0.6$ J·mol^{-1}·K^{-1}) (Figure 2). These activation parameters are essentially independent of concentration and solvent polarity (toluene-d_8 and THF-d_8), suggesting that the bromine atom intramolecularly rearranges over the three-membered ring without intermediate formation of the cyclotrigermenylium ion (Scheme 2). Similar NMR spectral changes were observed for **2a** ($E_a = 63.6$ kJ·mol^{-1}, $\Delta H^\ddagger = 61.1$ kJ·mol^{-1}, $\Delta S^\ddagger = 3.9$ J·mol^{-1}·K^{-1}) and **2c** ($E_a = 45.6$ kJ·mol^{-1}, $\Delta H^\ddagger = 43.5$ kJ·mol^{-1}, $\Delta S^\ddagger = -2.2$ J·mol^{-1}·K^{-1}). The activation parameters clearly show that the heavier halogen atom migrates more easily. In contrast to the dynamic behavior of **2**, the rearrangements of R_3C_3X (X = Cl, N_3) were shown to proceed according to the dissociation−recombination mechanism facilitated by the aromatic stabilization associated with the formed cyclopropenylium ion.[14]

The *cis*-bent geometry around the Ge═Ge double bond of the halogen-substituted cyclotrigermenes also affects the face selectivity of the Diels−Alder reaction with butadiene (Scheme 3).[8] The cyclotrigermenes **2a**−**2c** smoothly reacted with 2,3-dimethyl-1,3-butadiene at room temperature to give pale yellow crystals of **4a**−**4c** with a single stereoisomer (yields; **4a**: 91%, **4b**: 73%, **4c**: 83%), as determined by X-ray analyses.[9] Thus, the butadiene attacks the Ge═Ge double bond from the site of the more bulky $^tBu_3Si$ group in contrast to mesityl-substituted cyclotrigermene.[15,16]

Scheme 3



4a (X = Cl)
4b (X = Br)
4c (X = I)

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Supporting Information Available: The experimental procedures and spectral data of **2a**−**2c** and **4a**−**4c**, Tables of crystallographic data including atomic positional and thermal parameters for **2a**−**2c** and **4a**−**4c** (PDF). X-ray crystallographic files in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) For the recent reviews on metallenes and dimetallenes of Group 14 elements, see: (a) Weidenbruch, M. *Eur. J. Inorg. Chem.* **1999**, 373. (b) Power, P. P. *Chem. Rev.* **1999**, *99*, 3463. (c) Escudié, J.; Ranaivonjatovo, H.; *Adv. Organomet. Chem.* **1999**, *44*, 113.
(2) For cyclotrigermene and cyclotrigermenylium ion, see: (a) Sekiguchi, A.; Yamazaki, H.; Kabuto, C.; Sakurai, H.; Nagase, S. *J. Am. Chem. Soc.* **1995**, *117*, 8025. (b) Sekiguchi, A.; Tsukamoto, M.; Ichinohe, M. *Science* **1997**, *60*, 275. (c) Ichinohe, M.; Fukaya, N.; Sekiguchi, A. *Chem. Lett.* **1998**, 1045. (d) Sekiguchi, A.; Fukaya, N.; Ichinohe, M.; Takagi, N.; Nagase, S. *J. Am. Chem. Soc.* **1999**, *121*, 11587. (e) Sekiguchi, A.; Fukaya, N.; Ichinohe, M.; Ishida Y. *Eur. J. Inorg. Chem.* **2000**, 1155.
(3) For cyclotrigermenyl radical, see: Olmstead, M. M.; Pu, L.; Simons, R. S.; Power, P. P. *Chem. Commun.* **1997**, 1595.
(4) For cyclotrisilene, see: (a) Iwamoto, T.; Kabuto, C.; Kira, M. *J. Am. Chem. Soc.* **1999**, *121*, 886. (b) Ichinohe, M.; Matsuno, M.; Sekiguchi, A. *Angew. Chem., Int. Ed.* **1999**, *38*, 2194.
(5) For cyclotristannene, see: Wiberg, N.; Lerner, H.-W.; Vasisht, S.-K.; Wagner, S.; Karaghiosoff, K.; Nöth, H.; Ponikwar, W. *Eur. J. Inorg. Chem.* **1999**, 1211.
(6) For 1-disilagermirene and 2-disilagermirene, see: Lee, V. Ya.; Ichinohe, M.; Sekiguchi, A.; Takagi, N.; Nagase, S. *J. Am. Chem. Soc.* **2000**, *122*, 9034.
(7) For spiropentasiladiene, see: Iwamoto, T.; Tamura, M.; Kabuto, C.; Kira, M. *Science* **2000**, *290*, 504.
(8) For details of the experimental procedure and spectral data of **2a**−**2c** and **4a**−**4c**, see the Supporting Information.
(9) For details of the X-ray structure determinations of **2a**−**2c** and **4a**−**4c**, see the Supporting Information
(10) The Ge═Ge and Ge−Ge bond lengths of the three-membered skeleton for **2a** and **2c** are as follows; **2a**: 2.2723(8) (Ge═Ge), 2.4225(8) and 2.4293(8) Å (Ge−Ge); **2c**: 2.2721(6) (Ge═Ge), 2.4249(6) and 2.4287(6) Å (Ge−Ge).
(11) Goller, A.; Heydt, H.; Clark, T. *J. Org. Chem.* **1996**, *61*, 5840.
(12) The calculations were carried out using the Gaussian 98 program with effective core potentials and double-ζ (DZ) basis sets on Si, Ge, Cl, Br, and I (Wadt, W. R.; Hay, P. J. *J. Chem. Phys.* **1985**, *82*, 284) augmented by d-type polarization functions (d exponents 0.45 (Si), 0.246 (Ge), 0.75 (Cl), 0.389 (Br), 0.266 (I)). The 3-21G basis set was used for C and H. For example, the opitimized bond lengths of the three-membered ring for the real molecules are 2.311 (Ge═Ge), 2.466 and 2.469 Å (Ge−Ge) for **2b**; 2.310 (Ge═Ge), 2.470 and 2.474 Å (Ge−Ge) for **2c**. The *cis* folding angles are 36.1 and 10.6° for **2b**; 33.1 and 3.4° for **2c**.
(13) The calculated geometry around the Ge═Ge double bond for a real molecule $Ge_3(Si^tBu_3)_3Cl$ is *cis*-bent with folding angles of 31.5 and 4.2°, bond lengths of 2.310 (Ge═Ge), 2.470 and 2.461 Å (Ge−Ge). The model compound $Ge_3(SiH_3)_3Cl$ also shows the *cis*-bent geometry, and no energy minimum was found for the *trans*-bent one by the theoretical calculation, suggesting that the *trans*-bent geometry in **2a** is caused by a crystal-packing force.
(14) (a) Breslow, R.; Ryan, G.; Groves, J. T. *J. Am. Chem. Soc.* **1970**, *92*, 988. (b) Curci, R.; Lucchini, V.; Modena, G.; Kocienski, P. J.; Ciabattoni, J. *J. Org. Chem.* **1973**, *38*, 3149.
(15) For the recent paper on the facial stereoselectivity in the Diels−Alder reactions of 3-substituted cyclopropenes with butadienes, see: Xidos, J. D.; Gosse, T. L.; Burke, E. D.; Poirier, R. A.; Burnell, D. J. *J. Am. Chem. Soc.* **2001**, *123*, 5482.
(16) Fukaya, N.; Ichinohe, M.; Sekiguchi, A. *Angew. Chem. Int. Ed.* **2000**, *39*, 3881.

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