ORGANOMETALLICS

Volume 15, Number 14, July 9, 1996

Communications

Dichlorodigermacyclobutanes and Digermabicyclo[2.2.0]hexanes from the Reactions of [Tris(trimethylsilyl)methyl]chlorogermylene with Olefins

Toshiyuki Ohtaki and Wataru Ando*

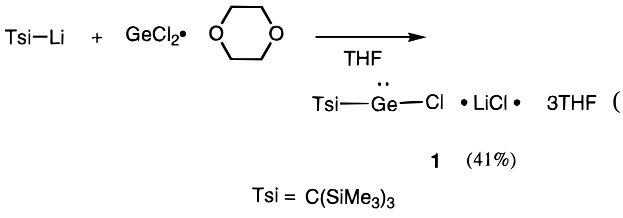
Department of Chemistry, University of Tsukuba, Tsukuba, Ibaraki 305, Japan

Received January 9, 1996[⊗]

*Summary: $GeCl_2$(dioxane) reacts with trisyllithium (($Me_3Si)_3SiLi$) to give a trisylchlorogermylene−LiCl−3THF complex (**1**), which is stable at room temperature. The reaction of **1** with olefins gave 1,2-dichloro-1,2-digermacyclobutanes (**2a**−**e**) exclusively. These were treated with Mg/$MgBr_2$ in the presence of olefins to give 1,4-digermabicyclo[2.2.0]hexane (**4**).*

The chemistry of germylenes has been studied extensively over the last two decades. We recently reported that the reaction of germylenes with olefins gives germacyclopropanes[1] and a 1,2-digermacyclobutane.[2] However, in most of the germylenes involved the two substituents were the same. In particular, there have been few reports of organohalogermylenes (R−Ge−X). Recently, Jutzi and co-workers have reported[3] the isolation of 2,4,6-tri-*tert*-butylphenyl (supermesityl = Mes*) and pentamethylcyclopentadienyl (Cp*) substituted chlorogermylenes. However, no details concerning their reactivity were provided. We report here the synthesis of the trisylchlorogermylene−LiCl−3THF complex (**1**; trisyl = tris(trimethylsilyl)methyl) as a germylene equivalent and its reactivity toward olefins. Reaction of **1** with olefins, followed by dehalogenation of the 1,2-dichloro-1,2-digermacyclobutanes produced, in the presence of olefins, gives 1,4-digermabicyclo[2.2.0]hexanes.

Reaction of the $GeCl_2$−dioxane complex with 1.2 equiv of trisyllithium (Tsi−Li) in THF at 0 °C gave **1** as pale yellow crystals (recrystallization from pentane at −78 °C, 41%) (eq 1).[4] Compound **1** is air-sensitive, both in solution and in the solid state. It dissolves in hydrocarbon solvents to give an orange solution. The ^1H NMR spectrum of **1** shows one signal for the trimethylsilyl group at δ 0.67 (in C_6D_6) and signals for THF, integration showing that the molar ratio of Tsi−Ge−Cl to THF is 1:3. In the ^{13}C NMR spectrum of **1**, besides the signals for the THF portion, signals for the trisyl groups appear at 0.94 and 5.39 ppm. Furthermore, the ^7Li NMR spectrum supported the existence (−0.20 ppm) of a lithium atom in the molecule.



(1)

[⊗] Abstract published in *Advance ACS Abstracts,* June 15, 1996.

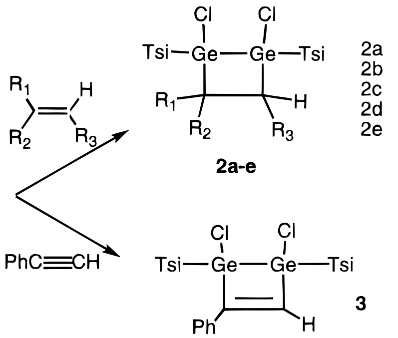
(1) Ando, W.; Ohgaki, H.; Kabe, Y. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 659 and references cited therein.

(2) Ohgaki, H.; Kabe, Y.; Ando, W. *Organometallics* **1995**, *14*, 2139.

(3) (a) Jutzi, P.; Leue, C. *Organometallics* **1994**, *13*, 2898. (b) Lange, L.; Meyer, B.; du Mout, W. W. *J. Organomet. Chem.* **1987**, *329*, C17. (c) Kohl, F. X.; Jutzi, P. *J. Organomet. Chem.* **1983**, *243*, 31. (d) Jutzi, P. *J. Organomet. Chem.* **1990**, *400*, 1. (e) Jutzi, P.; Becker, A.; Leue, C.; Stammler, H. G.; Neumann, B. *Organometallics* **1991**, *10*, 3838. (f) Jutzi, P.; Schmidt, H.; Neumann, B.; Stammler, H. G. *J. Organomet. Chem.* **1995**, *499*, 7.

S0276-7333(96)00014-3 CCC: $12.00

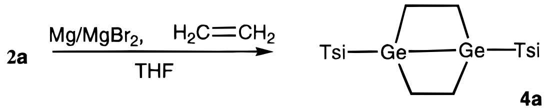
Scheme 1



The reaction of **1** with gaseous ethylene in hexane at room temperature produced 1,2-dichloro-1,2-digermacyclobutane (**2a**), a colorless and air-stable solid, in 54% yield.[5] The spectral data suggested the existence of only one isomer (cis or trans). A single-crystal X-ray diffraction study of **2a** confirmed its trans configuration. (However, a detailed structure could not be obtained because of severe disordering.) Furthermore, **1** also reacts with olefins such as propene, styrene, isobutene, and cyclopentene to give the corresponding 1,2-dichloro-1,2-digermacyclobutane derivatives (**2b**–**e**) in comparable yields (Scheme 1), perhaps with the trans configuration. However, **2b**,**c** have two isomers, respectively, which arise from the disposition of the methyl or perhaps groups on the cyclobutane ring.

As in the reaction of olefins, the reaction of **1** with acetylenes depended on the acetylene substituents. Only polymeric products were obtained (−78 °C to room temperature) in the reaction of acetylene itself. Disubstituted acetylenes, such as diphenylacetylene and diethylacetylene, did not react with **1** in hexane. The reaction of **1** with phenylacetylene gave 1,2-dichloro-1,2-digermacyclobut-3-ene (**3**) in 60% yield as a colorless solid which is stable toward atmospheric oxygen and moisture (Scheme 1).[6] In the ^{1}H NMR spectrum of **3**, one signal for the methylene proton on the ring at δ 7.84 and low-field ^{13}C resonances at 158.53 and 177.64 ppm due to the olefinic carbon in the cyclobutene ring support the 1,2-digermacyclobut-3-ene framework.

Scheme 2



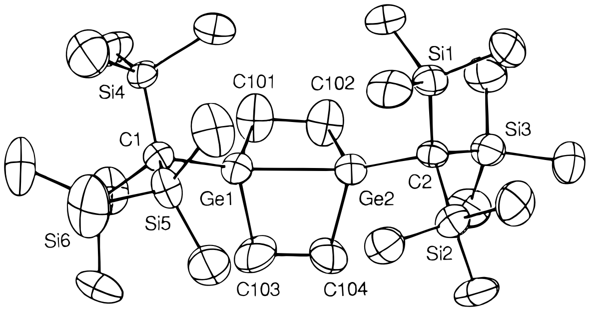


Figure 1. ORTEP drawing of **4a** showing 50% probability ellipsoids. Selected bond distances (Å) and angles (deg): Ge1−Ge2 = 2.513(1), Ge1−C101 = 2.01(1), Ge1−C103 = 2.03(1), Ge2−C102 = 2.01(1), Ge2−C104 = 2.01(1), C101−C102 = 1.55(2), C103−C104 = 1.60(3); C101−Ge1−Ge2 = 76.2(3), C103−Ge1−Ge2 = 76.7(3), C102−Ge2−Ge1 = 76.0(3), C104−Ge2−Ge1 = 77.1(3).

Treatment of **2a** with magnesium in THF in the presence of $MgBr_2$ (prepared by in situ reaction of magnesium with 1,2-dibromoethane) did not result in formation of a germanium−germanium-coupled product but gave instead the unexpected 1,4-digermabicyclo[2.2.0]hexane (**4a**) in 50% yield as colorless air-stable crystals (Scheme 2).[7] In the ^{1}H NMR spectrum of **4a**, the appearance of only one signal for the trimethylsilyl groups is in agreement with its symmetrical structure. The relatively low field ^{13}C NMR shift at 30.3 ppm for the methylene carbons supports the ring structure of **4a**. Crystals suitable for X-ray structural analysis were obtained by slow evaporation of a benzene solution of **4a** (Figure 1).[8] This compound has a rooflike conformation. However, no inversion was observed in VT-NMR spectroscopic experiments (room temperature to 80 °C).

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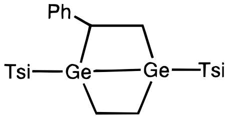
(4) Synthesis of [tris(trimethylsilyl)methyl]chlorogermylene: a solution of 4.00 g of $(Me_3Si)_3CH$ (17.2 mmol) in THF (40 mL) was added dropwise to 13.5 mL of halogen-free CH_3Li (in diethyl ether, 1.40 N, 18.9 mmol) (5 min). After removal of ether, the mixture was treated at reflux with an oil bath (70 °C, 3 h). The resulting deep yellow mixture was cannulated into a solution of $GeCl_2$−dioxane (3.50 g, 15.1 mmol) and 1 mL of Et_3N in 25 mL of THF at 0 °C. After the mixture was stirred for 1 h at ambient temperature, the solvent was removed under reduced pressure. The residual orange solid was extracted with 50 mL of pentane. Filtration through Celite afforded a clear orange solution. The latter was cooled to −78 °C to give a pale yellow solid (3.70 g, 41.0%).

(5) **2a**: colorless crystals; dec 202 °C (in air); ^{1}H NMR (C_6D_6) δ 0.50 (s, 54H), 2.43 (m, 4H); ^{13}C NMR (C_6D_6) δ 5.73 (SiMe), 26.82 (GeCSi), 34.78 ($GeCH_2$). Anal. Calcd for $C_{22}H_{58}Si_6Cl_2Ge_2$: C, 37.37; H, 8.27. Found: C, 37.74; H, 8.29. **2b** has two isomers; however, the minor species is not present in sufficient amount to allow its characterization by NMR spectroscopy (major:minor = 95:5). Therefore, NMR values for only the major source are reported. **2b**: colorless solid; ^{1}H NMR (C_6D_6) δ 0.47 (s, 27H), 0.49 (s, 27H), 1.59 (d, J = 7.5 Hz, 3H), 2.02−2.08 (m, 1H), 3.11−3.20 (m, 1H); ^{13}C NMR (C_6D_6) δ 5.91, 6.26 (SiMe), 22.24 ($-CH_3$), 26.33, 28.04 (GeCSi), 44.06 (CH_2), 52.03 (CH). Anal. Calcd for $C_{23}H_{60}Si_6Cl_2Ge_2$: C, 38.29; H, 8.38. Found: C, 38.30; H, 8.41. **2c** has two isomers, and the ratio of the two is 2:1: waxy white solid; ^{1}H NMR (C_6D_6) δ 0.36 (s, 27H, minor), 0.39 (s, 27H minor), 0.47 (s, 27H major), 0.49 (s, 27H, major), 2.95 (dd, 2H, minor), 3.15 (dd, 2H, major), 4.25 (dd, 1H, minor), 4.70 (dd, 1H, major), 7.25 (m, 10H); ^{13}C NMR (C_6D_6) δ 5.90, 5.97, 6.03, 6.11 (SiMe), 26.40, 28.82, 31.17, 32.05 (GeCSi), 42.76, 44.18 (CH_2), 55.52, 66.65 (CH), 126.52, 127.87, 128.52, 128.69, 128.88, 129.04, 142.35, 142.98 (Ph). Anal. Calcd for $C_{28}H_{62}Si_6Cl_2Ge_2$: C, 42.93; H, 7.98. Found: C, 42.99; H, 8.16. **2d**: waxy white solid; ^{1}H NMR (C_6D_6) δ 0.47 (s, 27H), 0.49 (s, 27H), 1.62 (s, 3H), 1.80 (s, 3H), 2.19 (d, 1H), 2.45 (d, 1H); ^{13}C NMR δ 6.12, 6.59 (SiMe), 12.15, 12.80 (GeCSi), 30.81, 32.42 ($-CH_3$), 51.18 (CH_2); 58.22 (C−Me). Anal. Calcd for $C_{24}H_{62}Si_6Cl_2Ge_2$: C, 39.20; H, 8.50. Found: C, 38.86; H, 8.44. **2e**: waxy white solid; ^{1}H NMR (C_6D_6) δ 0.48 (s, 27H), 1.17−1.43 (m, 2H), 1.82−2.35 (m, 4H), 3.10−3.45 (m, 2H); ^{13}C NMR δ 6.09, 6.31 (SiMe), 12.32, 14.16 (GeCSi), 31.14, 32.72, 33.12 (CH_2), 53.50, 64.06 (CH).

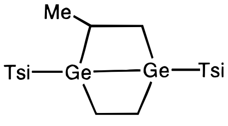
(6) For **3**: waxy white solid, ^{1}H NMR (C_6D_6) δ 0.42 (bs, 27H), 0.48 (s, 27H), 7.03−7.11 (m, 3H), 7.42−7.45 (m, 2H), 7.85 (s, 1H); ^{13}C NMR (C_6D_6) δ 5.83, 5.94 (SiMe); 22.54 (GeCSi); 127.02, 128.19, 128.54, 142.19 (Ph); 158.53, 177.64 (GeC=). Anal. Calcd for $C_{24}H_{62}Si_6Ge_2$: C, 43.38; H, 9.41. Found: C, 43.58; H, 9.46.

(7) Synthesis of **4a**: (1) Ethylene gas was introduced into a solution of 120 mg of **2** (0.17 mmol), Mg (20 mg), and $MgBr_2 \cdot Et_2O$ (70 mg) in 5 mL of THF. After the mixture was stirred for 2 h, the solvent was evaporated. The residue was extracted with 40 mL of hexane and purified by silica gel chromatography (69% yield). (2) Ethylene gas was introduced into a solution of 80 mg of **2** (0.13 mmol) in 8 mL of THF. Lithium naphthalenide (1.20 mL, 0.30 N in THF) was added dropwise to the solution at −78 °C. The resulting yellow solution was warmed to ambient temperature and stirred for 1 h. The solvent was removed, the residue was extracted with toluene and the product was isolated by preparative HPLC (68% yield): colorless crystals, dec 210 °C (in air); ^{1}H NMR (C_6D_6) δ 0.33 (s, 54 H), 2.23−2.36 (m, 8H); ^{13}C NMR (C_6D_6) δ 4.78 (SiMe), 14.01 (GeCSi), 30.14 (CH_2). Anal. Calcd for $C_{24}H_{62}Si_6Ge_2$: C, 43.38; H, 9.41. Found: C, 43.53; H, 9.36. The reaction of the $Mg/MgBr_2 \cdot Et_2O$ complex (no external ethylene present) with **2a** in THF gave a complex mixture of oligomers, decomposition products (mainly Tsi−H), and halogen-exchanged starting material. Neither the Ge−Ge-coupled dimer nor compound **4a** was obtained (by TLC or HPLC).

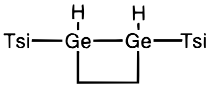
Although the Ge−C bond distances of 2.009−2.027 Å are in the normal range of Ge−C single bonds, the Ge−Ge and C−C bonds in the cyclic framework are comparatively longer than normal Ge−Ge and Ge−C bonds (2.513, 1.552, and 1.601 Å). However, the acute Ge−Ge−C angles in the ring (76.0−77.1°) serve to decrease the ring strain. Undoubtedly, the ethylene is derived from Mg debromination of 1,2-dibromoethane. It is noteworthy that when the reaction is carried out under an ethylene atmosphere the yield of **4a** is increased to 69%. In the presence of styrene and propene, the substituted 1,4-digermabicyclo[2.2.0]hexanes **4b**,**c** were obtained in 50% and 21% yield, respectively, together with 1,2-dihydro-1,2-digermacyclobutane (**5**, 23%). The reaction of **2a** with $Mg/MgBr_2$ in the presence of acetylene gave 1,2-divinyl-1,2-digermacyclobutane (**6**, 23%) as main product. The use of lithium powder or lithium naphthalenide in place of $Mg/MgBr_2$ produced **4a** in comparable yield.



4b



4c



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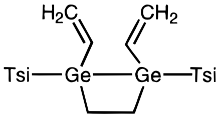

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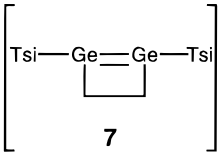

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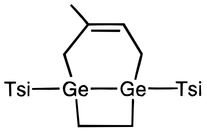

8

There are two possible mechanisms for the formation of adducts **4**−**6**. Magnesium and alkali metals could form 1,2-digermacyclobutene (**7**) by an electron transfer reaction of the 1,2-dihalogermane **2a**.[9] However, attempted trapping of **7** with ethanol at room temperature was not successful; no ethanol adduct was observed. On the other hand, the analogous dechlorination of **2a** in the presence of 2-methyl-1,3-butadiene, which is a trapping reagent[10] for a digermene (Ge═Ge), instead of ethylene gave the corresponding [2 + 4] adduct **8** in 23% yield.[11] An electron transfer reaction leading to the formation of a germyl radical is a possibility, at least in the reaction with olefins and butadiene.

Acknowledgment. This work was supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science, and Culture of Japan. We are grateful to Asai Germanium Research Institute for their generous gift of chlorogermanes.

Supporting Information Available: Text giving details of the X-ray crystal structure study and tables of crystal structure determination data, atomic coordinates, anisotropic thermal parameters, and bond lengths and angles for compound **4a** (19 pages). Ordering information is given on any current masthead page.

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(8) Crystallographic data for **4a**: $C_{24}H_{62}Si_6Ge_2$, triclinic, space group $P\bar{1}$, $a = 9.030(1)$ Å, $b = 13.675(1)$ Å, $c = 15.487(1)$ Å, $\alpha = 85.05(1)°$, $\beta = 88.86(1)°$, $\gamma = 73.98(1)°$, $V = 1831.2$ Å^3, ρ(calcd) = 1.20 g/cm^3, $\mu = 18.2$ cm^{-1}, $Z = 2$. The structure was solved from 5272 collected independent reflections ($2\theta \leq 50°$, $|F_o^2| > 3\sigma|F_o^2|$) measured on an Enraf-Nonius CAD4 diffractometer using Mo Kα irradiation and an $\omega - 2\theta$ scan. The structure was solved by direct methods, and all non-hydrogen atoms were refined anisotropically to $R = 0.069$ and $R_w = 0.086$. One trisyl group showed disordering; therefore, these extra atoms were omitted in Figure 1.

(9) Reductive dehalogenation of 1,2-dichloro-1,1,2,2-tetrakis(2,4,6-triisopropylphenyl)disilane using lithium naphthalenide gave a stable disilene: Watanabe, H.; Takeuchi, K.; Nakajima, K.; Nagai, Y.; Goto, M. *Chem. Lett.* **1988**, 1343.

(10) Barrau, J.; Escudie, J.; Satge, J. *Chem. Rev.* **1990**, *90*, 283 and references cited therein.

(11) **8**: white solid, sublimes at 205 °C (0.01 mmHg); ^{1}H NMR (C_6D_6) δ 0.37 (s, 27H), 0.38 (s, 27H), 1.80−2.64 (m, 8H), 2.03 (s, 3H), 5.73−5.78 (m, 1H); ^{13}C NMR (C_6D_6) δ 5.98 (q), 6.03 (q), 11.95 (s), 12.77 (s), 26.74 (t), 26.85 (q), 28.49 (t), 29.90 (t), 32.74 (t), 121.50 (t), 133.56 (s). Anal. Calcd for $C_{27}H_{66}Si_6Ge_2$: C, 46.03; H, 9.44. Found: C, 45.91; H, 9.35.