Heteroatom Chemistry
Volume 12, Number 4, 2001

Interconversion of Cyclotrimetallenes and Dihalocyclotrimetallanes Consisting of Group 14 Elements

Vladimir Ya. Lee, Tadahiro Matsuno, Masaaki Ichinohe, and Akira Sekiguchi

Department of Chemistry, University of Tsukuba, Tsukuba, Ibaraki 305-8571, Japan

Received 20 November 2000; revised 18 December 2000

ABSTRACT: *The 1- and 2-disilagermirenes and cyclotrisilene were reacted with carbon tetrachloride or 1,2-dibromoethane to give almost quantitatively the corresponding dihalocyclotrimetallane derivatives. The crystal structure of 1,2-dichloro-1,2,3,3-tetrakis-[di-tert-butyl(methyl)silyl]-1,2-disilagermirane showed a trans arrangement of the two chlorine atoms in the three-membered ring system. Reduction of the dihalocyclotrimetallanes with t-Bu_3SiNa quantitatively produced the corresponding starting cyclotrimetallenes.* © 2001 John Wiley & Sons, Inc. Heteroatom Chem 12:223–226, 2001

INTRODUCTION

The chemistry of highly strained cyclotrimetallanes consisting of group 14 elements heavier than carbon, which constitute now a well established class in the organometallic chemistry of group 14 [1], has attracted considerable attention because of their unique structures and great synthetic possibilities. Since the first discovery of cyclotrisilanes [2], cyclotrigermanes [3], and cyclotristannanes [4] by Masamune's group in the early 1980s, the chemistry of such molecules has been greatly developed during the last two decades concerning their synthesis, structural characterization, and reactivity. The reactivity of cyclotrimetallanes was found to be very interesting because they can serve as convenient precursors for both heavy carbene analogues and doubly-bonded species (dimetallenes). Mixed cyclotrimetallanes consisting of different group 14 elements are of special interest because one can imagine the generation of the unusual heteronuclear dimetallenes (such as germasilenes, germastannenes) from them. Nevertheless, only four examples of mixed cyclotrimetallanes have been reported so far: siladigermirane [5], two disilagermiranes [6,7], and germadistannirane [8]. Cyclotrimetallenes (R_4M_3, M = Si, Ge, Sn), that is, the compounds with endocyclic metal-metal double bonds, were prepared a few years ago: cyclotrigermenes were prepared in 1995 [9], cyclotrisilenes were prepared in 1999 [10,11], and cyclotristannene was prepared in 1999 [12]. Quite recently, we have succeeded in the preparation of the first mixed cyclotrimetallenes consisting of two different group 14 elements: 1- and 2-disilagermirenes [13]. These compounds exhibit an enhanced reactivity arising from the combination of highly reactive metal-metal double bond and highly strained three-membered ring skeleton in one mol-

---

Correspondence to: Akira Sekiguchi.

Contract Grant Sponsor: Ministry of Education, Science, and Culture of Japan.
Contract Grant Number: 10304051.
Contract Grant Sponsor: Ministry of Education, Science, and Culture of Japan.
Contract Grant Number: 12020209.
Contract Grant Sponsor: Ministry of Education, Science, and Culture of Japan.
Contract Grant Number: 12042213.

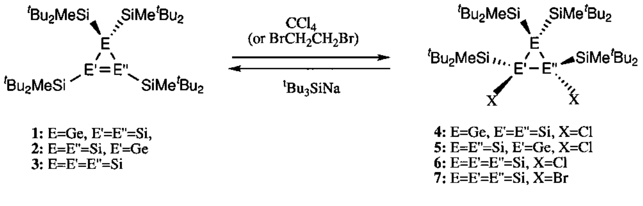
Dedicated to Prof. Naoki Inamoto on the occasion of his 72nd birthday.

ecule, which gives an access to the new cyclic and bicyclic compounds by the addition and cycloaddition reactions [14]. Here we report the reactivity of cyclotrimetallenes toward the halogenated hydrocarbons with the formation of the corresponding 1,2-dihalo derivatives, which in turn can be easily converted back to the starting cyclotrimetallenes under the action of the reducing agent like t-Bu_3SiNa.

RESULTS AND DISCUSSION

The reaction of the 1- and 2-disilagermirenes (**1**) and (**2**) with excess carbon tetrachloride results in the formation of the corresponding dichloroadducts in an almost quantitative yield, without any side products (Scheme 1). The cyclotrisilene (**3**) also readily reacts with carbon tetrachloride to give the 1,2-dichloroadduct [15]. This reaction proceeded immediately, even at low temperature, and during the reaction, the color of the reaction mixture changed from dark red to yellow, at which time the NMR spectra showed the absence of the starting material. Evaporation of excess CCl_4 left a yellow residue, which was found to be practically pure dichlorocyclotrimetallanes (**4**), (**5**), and (**6**). The reaction of cyclotrisilene **3** with 1,2-dibromoethane yielded the corresponding dibromocyclotrisilane (**7**). Of the two possible stereoisomers, only one was formed in the reaction of the cyclotrimetallenes with CCl_4 or 1,2-dibromoethane. All the new compounds **4–7** were isolated as air stable yellow crystals. The structures of compounds **4–7** were established on the basis of spectral data, elemental analysis, and X-ray crystallography.

For compounds **4**, **6**, and **7**, ^1H and ^{13}C NMR spectra showed the existence of two sets of signals from the different methyl groups and four resonances for the nonequivalent *tert*-butyl groups. This indicates that the two halogen atoms are in trans positions relative to each other. ^{29}Si NMR spectra revealed four resonances for **6** and **7** and three resonances for **4**, from which the two upfield signals (in the case of **4** only one) belong to the endocyclic silicon atoms, and the others belong to the silyl substituents. Compound **5** has no elements of symmetry and therefore produced more complicated spectra than compounds **4**, **6**, and **7**. Thus, the ^1H and ^{13}C NMR spectra of **5** showed three resonances (with two signals overlapping) for the methyl groups, and seven signals (with two signals overlapping) for the nonequivalent *tert*-butyl groups. The ^{29}Si NMR spectrum showed all the silicon atoms to be nonequivalent: -106.9 and -29.4 (endocyclic Si atoms), 21.7, 26.0, 27.0 and 39.3 ppm (exocyclic Si atoms).



SCHEME 1

The crystal structure of 1,2-dichloro-1,2,3,3-tetrakis[di-*tert*-butyl(methyl)silyl]-1,2-disilagermirane (**4**) was determined by X-ray analysis, as shown in Figure 1. The crystal structure data confirms that the two chlorine atoms are arranged in a trans configuration to each other, which is in agreement with the previously established trans geometry from the NMR data. Such geometry may be caused by the proposed radical mechanism [16] and the relative stability of the products. In the case of compound **4**, the endocyclic Si–Si and Si–Ge bond lengths of 2.342(2) and 2.467(1) Å, respectively, lie in a normal region and are quite similar to those of disilagermirane reported by Watanabe [7]. The two t-Bu_2MeSi groups attached to Si(1) and Si(2) atoms occupy the less hindered pseudo-equatorial positions, whereas the two chlorine atoms occupy the pseudo-axial positions, as determined by the angles between the three-membered ring plane and the Si–R vector (R = t-Bu_2MeSi and Cl): 146.2° for $^tBu_2MeSi$, and 115.7° for Cl. This geometry causes an elongation of Si–Cl bond (2.125(1) Å) relative to the average value of 2.05 Å [17].

It is interesting that the reactions of the dihalocyclotrimetallanes, **4–7**, with t-Bu_3SiNa, produced quantitatively the corresponding starting cyclotrimetallenes, **1**, **2**, and **3** (Scheme 1). The reactions

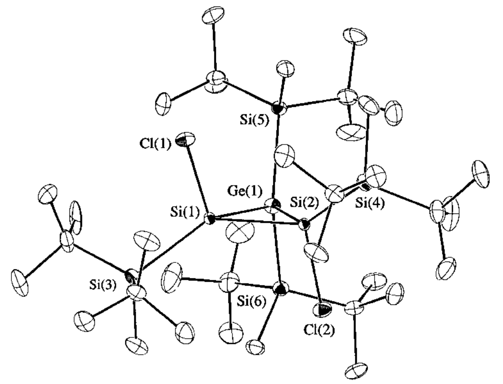


FIGURE 1 ORTEP drawing of **4** (hydrogen atoms are omitted for the clarity). Selected bond lengths (Å): Si1–Si2, 2.342(2); Si1–Ge1, 2.467(1); Si1–Si3, 2.416(1); Ge1–Si5, 2.469(1); Si1–Cl1, 2.125(1). Selected bond angles (°): Si1–Ge1–Si2, 56.7(0); Ge1–Si1–Si2 61.7(0).

proceeded very quickly and cleanly without the formation of any side products, except for $t\text{-Bu}_3\text{SiCl}$ (or $t\text{-Bu}_3\text{SiBr}$), and $t\text{-Bu}_3\text{SiSi-}t\text{-Bu}_3$. The reaction was easily monitored visually, by the change in color from yellow due to the compounds **4–7**, to an intense red, characteristic for the compounds **1–3**. It is likely that the reaction pathway includes an electron-transfer step with a halogen-sodium exchange to form an anionic intermediate, which then quickly undergoes elimination of NaX to form the final cyclotrimetallenes **1**, **2**, and **3**. Therefore, such dihalocyclotrimetallanes can be considered as an unusual but convenient and very effective source for the preparation of cyclotrimetallenes.

EXPERIMENTAL

General

All experiments were performed in an inert atmosphere of MBRAUN MB 150B-G glove-box and high-vacuum line techniques. All solvents were dried and degassed over potassium mirror in vacuo prior to use. NMR spectra were recorded on a Bruker AC-300 FT NMR spectrometer, and mass spectra were obtained on JEOL JMS SX-102 instrument. Cyclotrimetallenes were prepared according to the literature: 1- and 2-disilagermirenes [13a] and cyclotrisilene [11].

Typical Procedure for the Synthesis of Dihalocyclotrimetallanes (**4–7**)

An excess of dry CCl_4 (1 mL) was added through a vacuum transfer to a 1-disilagermirene **1** (35 mg, 0.04 mmol). Reaction immediately took place after melting of CCl_4 at low temperature, and the color of the reaction mixture was changed from dark red to yellow. The resulting 1,2-dichloro-1,2-disilagermirane **4** was isolated after evaporation of CCl_4 as yellow crystals in 98% (37.5 mg) yield, m.p. 221–223°C (dec.). Analytically pure sample can be obtained by the recrystallization from toluene. **4**: ^{1}H NMR δ (C_6D_6) 0.40 (s, 6H, Me), 0.51 (s, 6H, Me), 1.26 (s, 18H, *t*-Bu), 1.28 (s, 18H, *t*-Bu), 1.31 (s, 18H, *t*-Bu), 1.35 (s, 18H, *t*-Bu); ^{13}C NMR δ (C_6D_6) −3.5, 3.1, 23.0, 23.2, 23.3, 24.1, 30.3, 30.5, 31.0, 31.5; ^{29}Si NMR δ (C_6D_6) −34.0, 20.3, 36.2; Anal. calcd. for $\text{C}_{36}\text{H}_{84}\text{Cl}_2\text{GeSi}_6$: C, 52.15; H, 10.21. Found: C, 51.85; H, 10.53.

Compound **5**: bright-yellow crystals, 95% (36 mg), m.p. 140–142°C (dec.). ^{1}H NMR δ (C_6D_6) 0.43 (s, 3H, Me), 0.46 (s, 6H, Me), 0.57 (s, 3H, Me), 1.26 (s, 9H, *t*-Bu), 1.27 (s, 9H, *t*-Bu), 1.28 (s, 18H, *t*-Bu), 1.30 (s, 9H, *t*-Bu), 1.31 (s, 9H, *t*-Bu) 1.32 (s, 9H, *t*-Bu), 1.37 (s, 9H, *t*-Bu); ^{13}C NMR δ (C_6D_6) −3.0, −2.9, 2.9 (2C), 22.7, 23.0, 23.4, 23.5, 23.7 (2C), 23.8, 24.0, 29.9, 30.2, 30.4, 30.5, 31.06, 31.13, 31.6 (2C); ^{29}Si NMR δ (C_6D_6) −106.9, −29.4, 21.7, 26.0, 27.0, 39.3; Anal. Calcd. for $\text{C}_{36}\text{H}_{84}\text{Cl}_2\text{GeSi}_6$: C, 52.15; H, 10.21. Found: C, 51.86; H, 10.07.

Compound **6**: pale-yellow crystals, 91% (50 mg), m.p. 222°C (dec.). ^{1}H NMR δ (C_6D_6) 0.42 (s, 6H, Me), 0.46 (s, 6H, Me), 1.27 (s, 18H, *t*-Bu), 1.29 (s, 18H, *t*-Bu), 1.30 (s, 18H, *t*-Bu), 1.35 (s, 18H, *t*-Bu); ^{13}C NMR δ (C_6D_6) −3.3, 3.0, 22.8, 23.1, 23.3, 23.6, 30.2, 30.4, 31.0, 31.6; ^{29}Si NMR δ (C_6D_6) −127.1, −37.2, 21.9, 27.0; Anal. Calcd. for $\text{C}_{36}\text{H}_{84}\text{Cl}_2\text{Si}_7$: C, 55.11; H, 10.79. Found: C, 54.92; H, 10.90.

Compound **7**: pale-yellow crystals, 88% (40 mg), m.p. 207°C (dec.). ^{1}H NMR δ (C_7D_8) 0.42 (s, 6H, Me), 0.51 (s, 6H, Me), 1.24 (s, 18H, *t*-Bu), 1.287 (s, 18H, *t*-Bu), 1.294 (s, 18H, *t*-Bu), 1.35 (s, 18H, *t*-Bu); ^{13}C NMR δ (C_7D_8) −2.4, 4.5, 22.9, 23.7, 23.8, 23.9, 30.5, 30.6, 31.2, 31.9; ^{29}Si NMR δ (C_7D_8) −125.9, −53.2, 21.0, 27.8; Anal. Calcd. for $\text{C}_{36}\text{H}_{84}\text{Br}_2\text{Si}_7$: C, 49.50; H, 9.69. Found: C, 49.88; H, 9.92.

Typical Procedure for the Reduction of Dihalocyclotrimetallanes (**4–7**) with $t\text{-Bu}_3\text{SiNa}$

Dry THF-d_8 (0.5 mL) was introduced by a vacuum transfer to a mixture of dichlorodisilagermirane **5** (30 mg, 0.04 mmol) and $t\text{-Bu}_3\text{SiNa}$ (16 mg, 0.07 mmol). Reaction immediately proceeded even at low temperature, and the color of the reaction mixture became dark red, at which time the NMR spectra of the reaction mixture showed the quantitative formation of the sole compound: 2-disilagermirene **2** [13].

X-ray Crystallography of 1,2-Dichloro-1,2,3,3-tetrakis[di-tert-butyl(methyl)silyl]-1,2-disilagermirane (**4**)

A single crystal of **4** for X-ray diffraction was grown from a toluene solution. Diffraction data were collected at 120 K on a Mac Science DIP2030 Image Plate Diffractometer with a rotating anode (50 kV, 90 mA) employing graphite-monochromatized Mo Kα radiation (λ = 0.71070 Å). The structure was solved by the direct method and refined by the full-matrix least-squares method using SHELXL-97 program. Crystal data for **4** at 120 K: $\text{C}_{36}\text{H}_{84}\text{Cl}_2\text{GeSi}_6$, MW = 829.06, monoclinic, C2/c, a = 22.904(3), b = 13.034(1), c = 18.012(3) Å, β = 114.962(8)°, V = 4875(1) Å^3, Z = 4, D_{calcd} = 1.130 g/cm^3. The final R factor was 0.0663 for 5208 reflections with $I > 2\sigma(I)$ (wR_2 = 0.2038 for all data). GOF = 1.058.

REFERENCES

[1] (a) For the reviews on cyclotrimetallanes, see: Tsumuraya, T.; Batcheller, S. A.; Masamune, S. Angew Chem Int Ed Engl 1991, 30, 902; (b) Driess, M.; Grützmacher, H. Angew Chem Int Ed Engl 1996, 35, 275; (c) Weidenbruch, M. Chem Rev 1995, 95, 1479; (d) Weidenbruch, M. Eur J Inorg Chem 1999, 373.

[2] Masamune, S.; Hanzawa, W.; Murakami, S.; Bally, T.; Blount, J. F. J Am Chem Soc 1982, 104, 1150.

[3] Masamune, S.; Hanzawa, W.; Williams, D. J. J Am Chem Soc 1982, 104, 6137.

[4] Masamune, S.; Sita, L. R.; Williams, D. J. J Am Chem Soc 1983, 105, 630.

[5] Baines, K. M.; Cooke, J. A. Organometallics 1991, 10, 3419.

[6] Heine, A.; Stalke, D. Angew Chem Int Ed Engl 1994, 33, 113.

[7] Suzuki, H.; Okabe, K.; Uchida, S.; Watanabe, H.; Goto, M. J Organomet Chem 1996, 509, 177.

[8] Chaubon, M.-A.; Escudié, J.; Ranaivonjatovo, H.; Satgé, J. Chem Commun 1996, 2621.

[9] Sekiguchi, A.; Yamazaki, H.; Kabuto, C.; Sakurai, H.; Nagase, S. J Am Chem Soc 1995, 117, 8025.

[10] Iwamoto, T.; Kabuto, C.; Kira, M. J Am Chem Soc 1999, 121, 886.

[11] Ichinohe, M.; Matsuno, T.; Sekiguchi, A. Angew Chem Int Ed 1999, 38, 2194.

[12] Wiberg, N.; Lerner, H.-W.; Vasisht, S.-K.; Wagner, S.; Karaghiosoff, K.; Nöth, H.; Ponikwar, W. Eur J Inorg Chem 1999, 1211.

[13] (a) Lee, V. Ya.; Ichinohe, M.; Sekiguchi, A.; Takagi, N.; Nagase, S. J Am Chem Soc 2000, 122, 9034; (b) Lee, V. Ya.; Ichinohe, M.; Sekiguchi, A. Phosphorus Sulfur Silicon Relat Elem, in press.

[14] (a) Fukaya, N.; Ichinohe, M.; Sekiguchi, A. Angew Chem Int Ed 2000, 39, 3881; (b) Lee, V. Ya.; Ichinohe, M.; Sekiguchi, A. J Am Chem Soc; 2000, 122, 12604.

[15] Previously there was a short report on the preparation of 1,2-dichlorocyclotrisilane derivative by the reaction of 1-tris(*tert*-butyldimethylsilyl)silyl-2,3,3-tris(*tert*-butyldimethylsilyl)cyclotrisilene with CCl_4, see Ref. [10].

[16] Kira et al. reported the reaction of $(t\text{-BuMe}_2\text{Si})_2\text{Si}=\text{Si}(\text{SiMe}_2t\text{-Bu})_2$ with haloalkanes to produce the corresponding 1,2-dihaloderivatives (in the case of the reaction with CCl_4 and CBr_4). The reaction is explained by a radical mechanism. Iwamoto, T.; Sakurai, H.; Kira, M. Bull Chem Soc Jpn 1998, 71, 2741.

[17] Kaftory, M.; Kapon, M.; Botoshansky, M. The Chemistry of Organic Silicon Compounds; Rappoport, Z.; Apeloig, Y., Eds.; Wiley & Sons: New York, 1998; Vol. 2, Part 1, Chapter 5, p 240.