Unexpected Reactions of an Isolable Dialkylsilylene with Haloalkanes

Shintaro Ishida, Takeaki Iwamoto, Chizuko Kabuto, and Mitsuo Kira*
Department of Chemistry, Graduate School of Science, Tohoku University, Aoba-ku, Sendai 980-8578

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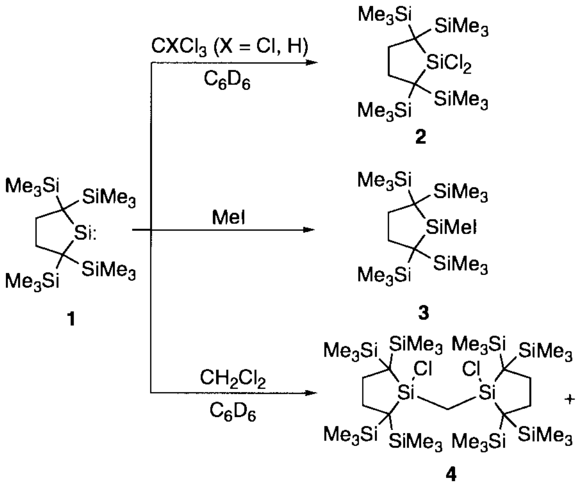
Reactions of an isolable dialkylsilylene with dichloromethane and (chloromethyl)cyclopropane occur in solution to afford the double silylene insertion product and an unusual 5-silaspiro[4.4]nonane derivative, respectively. The activation of the carbon–chlorine bonds due to the complexation of haloalkanes with the silylene may facilitate the nucleophilic attack of another silylene under the present reaction conditions.

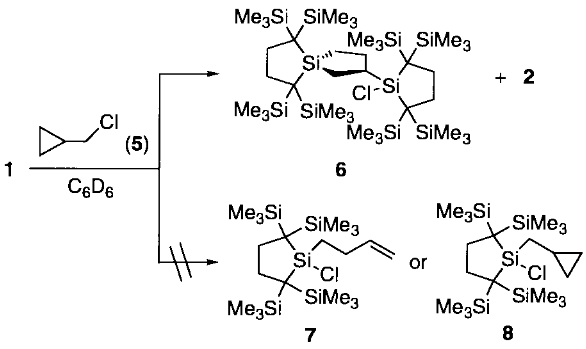
Although the reactions of silicon divalent compounds (silylenes) with various reagents such as alkenes, alkynes, alcohols, etc. have been extensively investigated,[1] less attention has been paid to the reactions of silylenes with haloalkanes,[2–5] in spite of the possible importance in the direct synthesis of alkylhalosilanes by the reactions of silicon with haloalkanes.[6] Typically, a photochemically generated transient silylene was found to react with 3-chloro-1-butene to give a mixture of the positional and geometrical isomers of the corresponding chloro(methylallyl)silanes.[2a] The reactions of transient silylenes with various haloalkanes have been explained by invoking zwitterionic intermediates (R_2Si^-–X^+R') formed at the initial stage.[2] Whereas several reactions of isolable silylenes, decamethylsilicocene and a cyclic diaminosilylene, with haloalkanes have been studied, the mechanisms have not been discussed in detail.[4,5] In the present paper, we have investigated the reactions of silylene **1**, 2,2,5,5-tetrakis(trimethylsilyl)silacyclopentane-1,1-diyl, which we have recently synthesized as the first isolable dialkylsilylene,[7] with various haloalkanes and have found unprecedented reaction modes of silylenes in the reactions of **1** with dichloromethane and (chloromethyl)cyclopropane. Although the whole feature of these reactions has not yet been disclosed, the present results suggest that the activation of a carbon–chlorine bond due to the complexation of a haloalkane with the silylene facilitates the nucleophilic attack of another silylene under the present reaction conditions.

As shown in Scheme 1, reactions of dialkylsilylene **1** with excess carbon tetrachloride and chloroform in benzene-d_6 occurred smoothly to give the corresponding dichlorosilane **2**[8] in 84 and 64% yields, respectively.[9] Silylene **1** readily reacted with excess iodomethane to afford the corresponding iodo(methyl)silane **3**[10] in 88% yield. Rather unexpectedly, the reaction of **1** with excess dichloromethane in benzene gave double silylene insertion product **4**[11] in 60% yield together with **2** (23% yield). No single silylene insertion product was observed in the reaction mixture even though the concentration of **1** was much lower than that of dichloromethane. A similar double insertion has been observed in the reaction of bis[di(trimethylsilyl)methyl]stannylene with dichloromethane.[12]

Scheme 1.



Scheme 2.



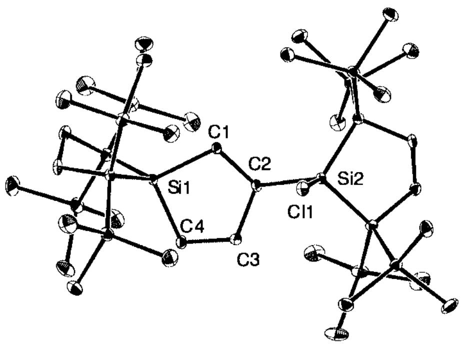


Figure 1. Molecular structure of **6**. Hydrogen atoms are omitted for clarity. The thermal ellipsoids are shown at 30% level.

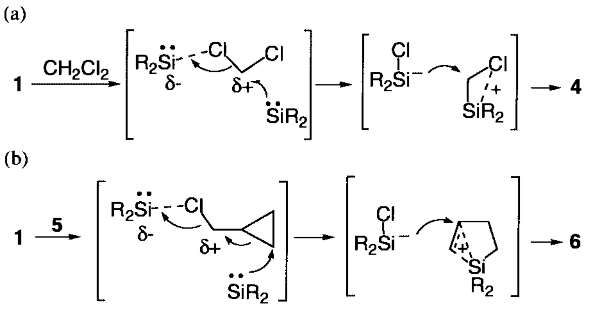
The reaction of **1** with excess (chloromethyl)cyclopropane **5** gave a 2 : 1 adduct **6**[13] in 70% yield together with **2** (15% yield); no 1:1 adducts such as **7** and **8** were detected (Scheme 2). The rather unusual structure of **6** was determined by NMR spectroscopy and X-ray structural analysis[14] (Figure 1).

Since small amounts of Cl_3CCCl_3 and HCl_2CCCl_2H were detected by mass spectrometry during the reactions of **1** with

CCl_4 and $CHCl_3$, respectively, a radical pathway would participate in part. The formation of dichlorosilane **2** in almost all reactions of **1** with chloroalkanes may be explained by this radical mechanism. Complexation of a haloalkane with **1**[15] weakens the carbon–chlorine bond to facilitate the homolytic cleavage, giving a pair of the corresponding carbon radical and chlorinated silyl radical, if the formed carbon radical is stabilized electronically. The chlorine-abstraction of the resulting silyl radical from chloroalkane affords **2**.[16]

However, the major reaction pathways of **1** with dichloromethane and (chloromethyl)cyclopropane **5** may not be explained by the above radical mechanism; in these reactions, a dichloromethane molecule reacts with two silylene molecules even in the presence of a large excess amount of dichloromethane. As shown in Scheme 3(a), the methylene carbon in the initial silylene–dichloromethane complex is attacked by another silylene to form a chlorosilyl anion and a (chloromethyl)silyl cation stabilized by intramolecular complexation, followed by the nucleophilic attack of the silyl anion to the chloromethyl carbon to afford **3**. Similarly, in the reaction of **1** with (chloromethyl)cyclopropane **5**, the reaction of the initial complex with an extra **1** affords the chlorosilyl anion and the corresponding 3-butenylsilyl cation with intramolecular π complexation, which reacts with the chlorosilyl anion to afford the final product **6**, as shown in Scheme 3(b). The reaction mode of **1** with **5** is quite different from that of the photochemically generated transient silylene Ph(Me$_3$Si)Si**:** with **5** observed by Ishikawa, Kumada, et al.;[2c] in the latter reaction, the silylene simply inserts to the C–Cl bond of **5** to give the corresponding (cyclopropylmethyl)chlorosilane without formation of any ring-opened products. The remarkable difference between the two reactions may be rationalized by the difference in the silylene concentration; the concentration of **1** was ca. 0.2 mol L^{-1}, while the steady-state concentration of Ph(Me$_3$Si)Si**:** was not known but should be far smaller than 0.2 mol L^{-1}. In the reaction of Ph(Me$_3$Si)Si**:** with **5**, the intra-complex nucleophilic attack of the silylene to the chlorinated carbon in the initial complex would occur exclusively to afford the simple insertion product.

Scheme 3.



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Dedicated to Professor Hideki Sakurai on the occasion of his 70th birthday.

References and Notes

1 For a recent review of silylenes: P. P. Gaspar and R. West, in "The Chemistry of Organic Silicon Compounds" 2nd ed., ed. by Z. Rappoport and Y. Apeloig, John Wiley & Sons, New York (1999), Part 3, Chap. 43, p 2463.

2 a) M. Ishikawa, K. Nakagawa, and M. Kumada, *J. Organomet. Chem.*, **214**, 277 (1981). b) M. Ishikawa, K. Nakagawa, S. Katayama, and M. Kumada, *J. Am. Chem. Soc.*, **103**, 4170 (1981). c) M. Ishikawa, K. Nakagawa, S. Katayama, and M. Kumada, *J. Organomet. Chem.*, **216**, C48 (1981).

3 R. Nakao, K. Oka, T. Dohmaru, Y. Nagata, and T. Fukumoto, *J. Chem. Soc., Chem. Commun*., **1985**, 766; K. Oka and R. Nakao, *J. Organomet. Chem.*, **390**, 7 (1990).

4 P. Jutzi, U. Holtmann, D. Kanne, C. Kruger, R. Blom, R. Gleiter, and I. Hyla-Krypsin, *Chem. Ber.*, **122**, 1629 (1989).

5 T. A. Schmedake, M. Haaf, Y. Apeloig, T. Müller, S. Bukalov, and R. West, *J. Am. Chem. Soc.*, **121**, 9749 (1999).

6 B. Pachaly and J. Weis, in "Organosilicon Chemistry. III", ed. by N. Auner and J. Weis, Wiley-VCH: Weinheim (1998), p 478.

7 M. Kira, S. Ishida, T. Iwamoto, and C. Kabuto, *J. Am. Chem. Soc.*, **121**, 9722 (1999).

8 M. Kira, T. Hino, Y. Kubota, N. Matsuyama, and H. Sakurai, *Tetrahedron Lett*., **29**, 6939 (1988).

9 All the reactions of **1** with haloalkanes were performed with standard vacuum-line technique. Yields of the products were determined by ^{1}H NMR spectroscopy using 1,2,4,5-tetramethylbenzene as an internal standard. Typically, to silylene **1** (28 mg, 0.08 mmol) frozen at 77 K in an NMR tube was transferred carbon tetrachloride (0.05 mL) in C_6D_6 (0.5 mL) by distillation. The color of the solution disappeared immediately during melting of the mixture.

10 **3**: a colorless waxy solid; ^{1}H NMR (C_6D_6, δ) 0.15 (s, 18H), 0.34 (s, 18H), 1.31 (s, 3H), 1.7–2.0 (m, 4H); ^{13}C NMR (C_6D_6, δ) 1.6 (SiMe$_3$), 1.6 (SiMe$_3$), 14.7 (C), 16.1 (CH$_3$), 33.6 (CH$_2$) ; ^{29}Si NMR (C_6D_6, δ) 3.8 (SiMe$_3$), 6.1 (SiMe$_3$), 28.8 (SiMeI); MS (EI, 70 eV) m/z (%) 449 (21, M^+–15), 387 (65), 229 (29), 225 (31), 73 (100).

11 **4**: colorless crystals; mp 246 °C; ^{1}H NMR (CDCl$_3$, 313 K, δ) 0.26 (brs, 36 H), 0.27 (brs, 36 H), 1.43 (s, 2 H, Si–C$\underline{H}_2$–Si), 1.9–2.4 (m, 8 H); ^{13}C NMR (CDCl$_3$, 313 K, δ) 4.6 (CH$_3$), 5.1 (CH$_3$), 15.4 (C), 20.2(Si–$\underline{C}$H$_2$–Si), 34.3 (CH$_2$); ^{29}Si NMR (CDCl$_3$, 313 K, δ) 2.7 (SiMe$_3$), 5.7 (SiMe$_3$), 43.5 ($\underline{Si}$–Cl); MS (EI, 70 eV) m/z (%) 813 (4, M^+ – Me), 585 (9), 407 (44), 73 (100); Anal. Calcd for $C_{33}H_{82}Si_{10}Cl_2$: C: 47.71, H: 9.95%. Found: C, 47.52; H, 9.67%.

12 M. J. S. Gynane, M. F. Lappert, S. J. Miles, A. J. Carty, and N. J. Taylor, *J. Chem. Soc., Dalton. Trans.*, **1977**, 2009.

13 **6**: colorless crystals; mp 328 °C; ^{1}H NMR (CDCl$_3$, 313 K, δ) 0.13 (s, 27H), 0.17 (s, 9H), 0.20 (s, 9H), 0.21 (s, 27H), 0.70 – 0.90 (m, 1H), 1.32 – 1.45 (m, 6H), 1.70 – 2.10 (m, 8H); ^{13}C NMR (CDCl$_3$, 313 K, δ) 3.98 (CH$_3$), 3.99 (CH$_3$), 4.06 (CH$_3$), 4.14 (CH$_3$), 4.57 (CH$_3$), 4.62 (CH$_3$), 4.7 (CH$_3$), 4.8 (CH$_3$), 10.3 (C), 10.6 (C), 11.8 (C), 14.4 (C), 17.7 (CH$_2$), 18.3 (CH$_2$), 29.9 (CH$_2$), 31.0 (CH), 32.8 (CH$_2$), 33.6 (CH$_2$), 34.2 (CH$_2$), 34.8 (CH$_2$); ^{29}Si NMR (CDCl$_3$, 313 K, δ) 2.4 (SiMe$_3$), 2.9 (SiMe$_3$), 3.3 (SiMe$_3$), 3.3 (SiMe$_3$), 3.3 (SiMe$_3$), 3.9 (SiMe$_3$), 5.0 (SiMe$_3$), 5.3 (SiMe$_3$), 41.1 (Si), 55.4 ($\underline{Si}$–Cl); MS (EI, 70 eV) m/z (%) 834 (100, M^+), 819 (31), 407 (87), 373 (87), 73 (64); Anal. Calcd for $C_{36}H_{87}ClSi_{10}$: C, 51.70; H, 10.48%. Found: C, 51.66; H, 10.20%.

14 Crystal data for **6** (150 K): $C_{36}H_{87}ClSi_{10}$, fw = 836.39, orthorhombic, Space group $P2_12_12_1$(#19), a = 15.0119(4) Å, b = 17.1085(5) Å, c = 19.4532(3) Å, V = 4996.2(2) A^3, D_{calcd} = 1.112 g·cm^{-3}, Z = 4, R = 0.041 (for I>2σ(I)), wR_2 = 0.140 (for all data).

15 No significant interaction between silylene **1** with chlorobenzene in solution was observed even at low temperatures as investigated by NMR and UV–vis spectroscopies. The silylene–haloalkane complexes may not have a strong silicon–halogen bond as expected in the zwitterionic intermediates proposed previously.[2,3] For silylene–base complexes, see: J. M. Jasinsk, *J. Chem. Phys*., **86**, 3057 (1986); W. Ando, K. Hagiwara, and A. Sekiguchi, *Organometallics*, **6**, 2270 (1987); G. R. Gillette, G. H. Gordon, and R. West, *Organometallics*, **6**, 2617 (1987); W. Ando, A. Sekiguchi, K. Hagiwara, A. Sakakibara, and H. Yoshida, *Organometallics*, **7**, 558 (1988); M. Kira, T. Maruyama, and H. Sakurai, *Heteroat. Chem*., **5**, 305 (1994); N. Takeda, H. Suzuki, N. Tokitoh, R. Okazaki, and S. Nagase, *J. Am. Chem. Soc.*, **119**, 1456, (1997); J. Belzner and H. Ihmels, *Adv. Organomet. Chem*., **43**, 1 (1999).

16 A similar mechansim has been proposed for the reactions of transient dimethylgermylene with CCl_4 and other haloalkanes, on the basis of CIDNP experiments: J. Kocher, M. Lehnig, and W. P. Neumann, *Organometallics,* **7**, 1201 (1988).