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Phosphonium Chloride Induced Dichlorosilylene Transfer from Trichlorosilane

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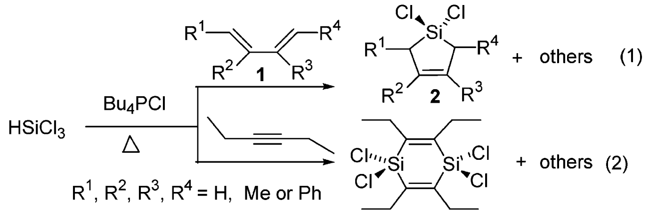
Summary: Heating trichlorosilane with conjugated dienes or an acetylene solution at 150 or 180 °C in the presence of a catalytic quantity of tetrabutylphosphonium chloride resulted in elimination of HCl and dichlorosilylene transfer to the unsaturated substrates to afford silacyclopentenes or 1,4-disilacyclohexa-2,5-dienes, respectively, in good to excellent yields. The trapping reaction with hex-3-yne gave 1,1,4,4-tetrachloro-2,3,5,6-tetraethyl-1,4-disilacyclohexa-2,5-diene in 79% yield, and its structure was determined by X-ray crystallography.

The chemistry of silylenes has seen remarkable development in recent decades and impacted greatly on organosilicon chemistry.[1] Although the thermolysis of polysilanes is widely used to generate unstable silylene intermediates,[2] dichlorosilylene can only be generated by heating hexachlorodisilane or chloromonosilanes at temperatures well above 500 or 900 °C, respectively, in the gas phase.[3] In another unrelated experiment, hexachlorodisilane was heated in the presence of an amine at 80−100 °C to give polydichlorosilanes, the synthesis of which was postulated to occur via dichlorosilylene.[4] Additionally, Benkeser attempted to trap the dichlorosilylene with diphenylacetylene[5a] in the amine-catalyzed coupling reaction of activated organic chlorides with trichlorosilane[5] but was not successful. Karsch and co-workers also reacted polarized 1,3-diazabutenes with $HSiCl_3$ to obtain [4 + 1] cycloadducts[6] but did not explain the product formation in terms of a dichlorosilylene reaction.[6] Dichlorosilylene was generated at room temperature by α-elimination of trimethylchlorogermane from (trichlorosilyl)trimethylgermane and trapped with *p*-phosphanyl phosphaalkenes.[7] In view of these earlier reports, we wish to report the surprisingly facile transfer of dichlorosilylene from $HSiCl_3$ to appropriate substrates at 150 or 180 °C in the presence of catalytic quantities of tetrabutylphosphonium chloride ($[Bu_4P]Cl$). Dichlorosilylene reactions with conjugated dienes (**1**) and acetylenes proceeded as shown in eqs 1 and 2, giving products in good to excellent yields. The possibility of the intermediary of $[:SiCl_2]$ is discussed.



Recently, we communicated the novel phosphonium chloride catalyzed dehydrohalogenative Si−C coupling reaction of alkyl chlorides with $HSiCl_3$, which gives organotrichlorosilanes in excellent yields.[8] This reaction works effectively with activated and nonactivated organic halides at temperatures ranging from 130 to 170 °C. For the mechanism, we proposed an intermediate pentacoordinated hydridotetrachlorosilane anion, $[HSiCl_4]^-$ (**I**), formed by the interaction of $[Bu_4P]Cl$ with $HSiCl_3$, which loses hydrogen chloride to give a tetrabutylphosphonium cation/trichlorosilyl anion pair (**II**).[8] Then the trichlorosilyl anion of the intermediate **II** attacks the alkyl chloride to produce the Si−C coupling product.[8] As an alternative, the possibility exists for the trichlorosilyl anion to lose chloride ion to give the intermediate dichlorosilylene, $[:SiCl_2]$. The latter then could insert into the C−Cl bond to form the Si−C-coupled products.[9] To test whether dichlorosilylene is generated by heating $HSiCl_3$ in the presence of $[Bu_4P]$-

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(3) (a) Sirtl, E.; Reuschel, K. *Z. Anorg. Allg. Chem*. **1964**, *332*, 113. (b) Chernyshev, E. A.; Komalenkova, N. G.; Bashkirova, S. A. *J. Organomet. Chem*. **1984**, *271*, 129. (c) Walker, K. L.; Jardine, R. E.; Ring, M. A.; O'Neal, H. E. *Int. J. Chem. Kinet*. **1998**, *30*, 69.

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(5) (a) Benkeser, R. A. *Acc. Chem. Res*. **1971**, *4*, 94. (b) Benkeser, R. A.; Smith, W. E. *J. Am. Chem. Soc*. **1968**, *90*, 5307. (c) Benkeser, R. A.; Gaul, J. M.; Smith, W. E. *J. Am. Chem. Soc*. **1969**, *91*, 3666.

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(9) (a) Timms, P. L. *Inorg. Chem*. **1968**, *7*, 387. (b) Chernyshev, E. A.; Komalenkova, N. G.; Kapitova, L. A.; Bashkirova, S. A *Zh. Obshch. Khim*. **1996**, *66*, 1141. (c) Ishida, S.; Iwamoto, T.; Kabuto, C.; Kira, M. *Chem. Lett*. **2001**, 1102. (d) Moser, D. F.; Bosse, T.; Olson, J.; Moser, J. L.; Guzei, I. A.; West, R. *J. Am. Chem. Soc*. **2002**, *124*, 4186.

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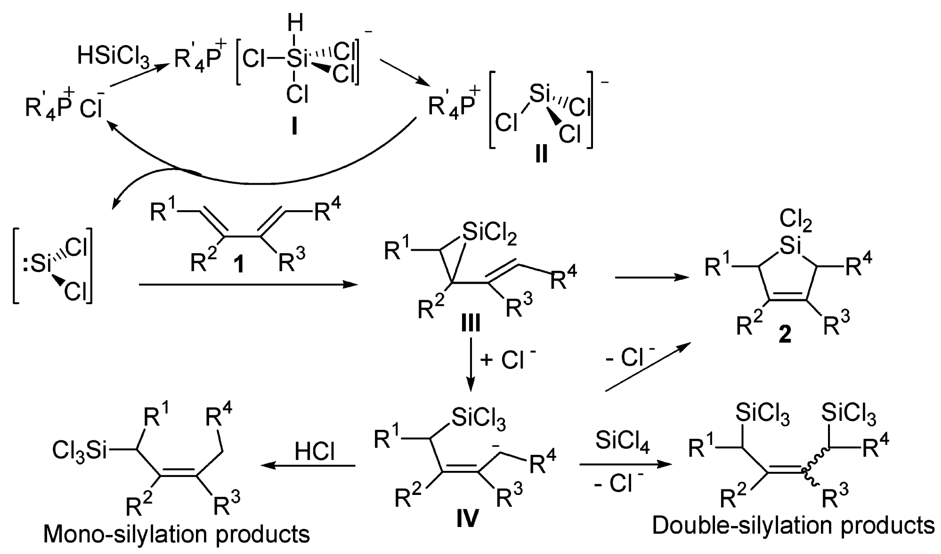
Scheme 1. Proposed Mechanism for the Formation of 2



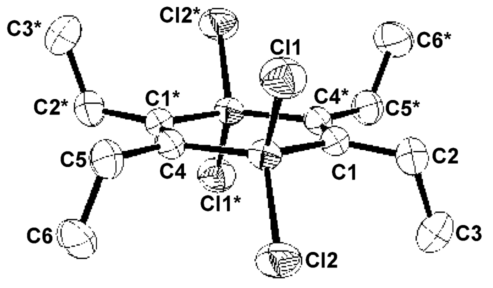
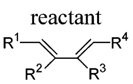
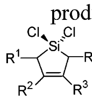


Figure 1. Molecular structure of **3**. Thermal ellipsoids are drawn at the 30% level (hydrogen atoms are omitted for clarity). Selected bond distances (Å) and angles (deg): C1–C4*, 1.344(9); Si1–C1, 1.851(6); Si1–Cl1, 2.050(2); C1*–Si1*–C4*, 117.4(3); C1–C4*–Si1*, 121.1(5); Cl1*–Si1*–Cl2*, 105.02(11); C1*–Si1*–Cl1*, 107.7(2).

Cl, we reacted $HSiCl_3$ with 2,3-dimethylbutadiene (**1c**), known as a good trapping agent of silylene,[1] at 150 °C in the presence of 10 mol % of $[Bu_4P]Cl$.[10] The dichlorosilylene-trapping product, 1,1-dichloro-3,4-dimethylsilacyclopent-3-ene (**2c**),[11] was obtained in 92% yield along with a 2:3 mixture of (*E*)- and (*Z*)-1,4-bis(trichlorosilyl)-2,3-dimethylbut-2-enes[12] as minor products. The results obtained in this reaction with a variety of conjugated dienes are listed in Table 1.

Table 1. Reaction of Dienes 1 with $HSiCl_3$ [a]

reactant 					reaction conditions		products (%)[b] 	
					temp.	time	**2**	
1	R^1	R^2	R^3	R^4	(°C)	(h)		others
1a	H	H	H	H	150	2	**2a**,[13] 68[c]	25[d]
1b	H	Me	H	H	150	5	**2b**,[14] 94 (87)[c]	
1c	H	Me	Me	H	150	5	**2c**,[11] 92 (85)[c]	
1d	Me	H	H	Me	180	8	(*Z*)-**2d**,[15] 83	
1e	H	Ph	Ph	H	150	5	**2e**,[16] 90	

[a] The reaction was carried out using a 40:10:1 mol ratio of $HSiCl_3$ to **1** to catalyst. [b] Yields were determined by GLC using *n*-dodecane as an internal standard. [c] Isolated yield. [d] Crotyltrichlorosilane and a 48:52 mixture of (*E*)- and (*Z*)-1,4-bis(trichlorosilyl)-2-butenes were obtained in 20 and 5% yields as byproducts, respectively.

As shown in Table 1, the reaction with butadiene itself (**1a**) gave the silylene-trapping product **2a** in 68% isolated yield, along with a mixture of (*E*)- and (*Z*)-1,4-bis(trichlorosilyl)but-2-enes[17] (5%) and crotyltrichlorosilane[17] (20%) as minor products. The reactions with other dienes **1b**–**e** gave **2b**–**e** in higher yields (83–94%), and the total yield of mono- and 1,4-bis(trichlorosilyl)-2-butene byproducts was less than 10%. Generally, internal methyl-substituted dienes **1b**,**c** reacted more rapidly and gave higher yields of **2** than did the terminal methyl-substituted diene **1d**. It is known that a silylene intermediate can be inserted into Si–Cl[7b] or Si–H bonds[18] to form disilanes. However, the insertion products of disilanes or polysilanes were not observed,

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[10] As a representative for the reaction of dienes with $HSiCl_3$, its reaction with **1b** with $HSiCl_3$ is described as follows: a 25 mL dried stainless steel bomb equipped with a valve was charged with $[Bu_4P]Cl$ (0.43 g, 1.46 mmol), **1b** (1.00 g, 14.68 mmol), $HSiCl_3$ (7.96 g, 58.77 mmol), and *n*-dodecane as an internal standard under a dry nitrogen atmosphere. After the valve was closed, a 5 h reaction in a heating oven at 150 °C gave **2b** and a 2:3 mixture of (*E*)- and (*Z*)-1,4-bis(trichlorosilyl)-2-methyl-2-butene in 94 and 4% yields, respectively, using GLC. Subsequently, the reaction mixture was fractionally distilled to give **2b** (2.14 g, 12.81 mmol) in 87% yield. Data for **2b**: bp 157–158 °C; ^1H NMR ($CDCl_3$) δ 1.79 (s, 2H, $=CHCH_2Si$), 1.81 (s, 3H, CH_3), 1.88 (s, 2H, $SiCH_2C=$), (m, 1H, $=CH$); ^{13}C NMR ($CDCl_3$) δ 23.10, 23.74, 27.00, 123.03, 138.73. Data for other minor products and the reactions with **1a**,**c**–**e** in detail are described in the Supporting Information.

[11] Barton, T. J.; Tillman, N. *J. Am. Chem. Soc.* **1987**, *109*, 6711.

[12] 1,4-Bis(trichlorosilyl)-2,3-dimethylbut-3-enes obtained as minor products from a reaction of **1c** with trichlorosilane were characterized indirectly by comparing the NMR spectra of their methylation products with those in the following reference: Dunogues, J.; Calas, R.; Dedier, J.; Pisciotti, F. *J. Organomet. Chem.* **1970**, *25*, 51. Data for the methylation of **2c** in detail are given in the Supporting Information.

[13] Damrauer, R.; Simon, R.; Laporterie, A.; Manuel, G.; Park, Y. T.; Weber, W. P. *J. Organomet. Chem.* **1990**, *391*, 7.

[14] Chernyshev, E. A.; Komalenkova, N. G.; Yakovleva, G. N.; Bykovenko, V. G.; Shcherbinin, V. V.; Belokon, A. I. *Zh. Obshch. Khim.* **2001**, *71*, 1438.

[15] The geometric structure for **2d** was characterized indirectly by comparing the NMR spectra of the methylation products with those in the following reference: Lei, D.; Hwang, R.-J.; Gaspar, P. P. *J. Organomet. Chem.* **1984**, *271*, 1. Data for the methylation of **2d** in detail are given in the Supporting Information.

[16] Data for **2e**: mp 86–87 °C; ^1H NMR ($CDCl_3$) δ 2.52 (s, 4H, CH_2), 7.04–7.17 (m, 10H, phenyl *H*); ^{13}C NMR ($CDCl_3$) δ 30.18 ($SiCH$), 126.82, 12.97, 128.67, 136.08 (phenyl *C*), 140.49 ($C=$). Anal. Calcd for $C_{16}H_{14}Cl_2Si$: C, 62.95; H, 4.62. Found: C, 63.21; H, 4.69.

[17] Furuya, N.; Sukawa T. *J. Organomet. Chem.* **1975**, *96*, C1.

[18] Wiberg, N.; Niedermayer, W. *J. Organomet. Chem.* **2001**, *628*, 57.

probably due to their decomposition under our reaction conditions.[19]

Among the known silylene trapping agents, alkynes are known to be as effective as conjugated dienes.[1b,20] In view of this, the $HSiCl_3$/[Bu_4P]Cl reaction was carried out in the presence of hex-3-yne. This reaction gave the expected silylene-trapping product, 1,1,4,4-tetrachloro-2,3,5,6-tetraethyl-1,4-disilacyclohexa-2,5-diene (**3**), in 79% yield.[21] The X-ray diffraction structure of the six-membered-ring compound **3** showed it to be in the chair conformation with two carbon−carbon double bonds of length 1.34 Å. Other silicon−carbon (1.85 Å) and silicon−chlorine (2.05 Å) bond lengths were within the expected range (Figure 1).

On the basis of our results, we propose a mechanism for the [Bu_4P]Cl-catalyzed dichlorosilylene generation and the trapping reaction with **1**, as shown in Scheme 1. [Bu_4P]Cl interacts with $HSiCl_3$ to form the intermediate **I**, which loses hydrogen chloride upon heating to give the intermediate **II**.[8] Intermediate **II** subsequently loses a chloride ion to produce dichlorosilylene, [:$SiCl_2$], and to regenerate the [Bu_4P]Cl catalyst. This [:$SiCl_2$] adds to carbon−carbon double bonds of conjugated dienes **1** to form the silacyclopropane intermediate **III**, as is the case of [:CCl_2], which undergoes a ring expansion with the other vinyl group to give the 1-silacyclopent-3-ene **2**.[1b] In an alternative pathway, the intermediates **III** could be attacked by Cl^-, to give the ring-opened 1-trichlorosilyl-substituted butenyl anion **IV**. This intermediate **IV** then could react with hydrogen chloride to give a single-silylation product or with tetrachlorosilane to give a double-silylation product.

We are presently investigating the utilization of dichlorosilylene for the preparation of a variety of organochlorosilanes. These results will be disclosed in a future paper.

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Supporting Information Available: Text and figures giving synthetic and spectral details for compounds **2a**−**e**, **3**, and other byproducts and tables and figures giving X-ray crystallographic details for **3**. This material is available free of charge via the Internet at http://pubs.acs.org.

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[19] Hexachlorodisilane decomposed into tetrachlorosilane and polysilanes in the presence of tetrabutylphosphonium chloride at the reaction temperatures.

[20] (a) Atwell, W. H.; Weyenburg, D. R. *J. Organomet. Chem.* **1966**, *5*, 5940. (b) Atwell, W. H.; Weyenburg, D. R. *J. Am. Chem. Soc.* **1968**, *90*, 3438.

[21] Using a procedure similar to that described in the reaction of **1b** with $HSiCl_3$, the reaction of 3-hexyne (1.00 g, 12.17 mmol) with $HSiCl_3$ (6.60 g, 48.70 mmol) in the presence of [Bu_4P]Cl (0.36 g, 1.22 mmol) at 180 °C for 10 h gave **3** (79%) and a mixture of (*Z*)-3,4-bis(trichlorosilyl)hex-3-ene and 3,4-bis(trichlorosilyl)hexanes as minor products. The product **3** (1.61 g, 73%) was isolated by recrystallization from the hexane solution. Colorless single crystals of **3** for X-ray diffraction study were grown from an *n*-hexane solution at −23 °C, and the ORTEP plot is depicted in Figure 1. Data for **3**: mp 67−68 °C; ^1H NMR ($CDCl_3$) δ 1.17−1.22 (t, 12H, CH_3), 2.50−2.58 (q, 8H, CH_2); ^{13}C NMR ($CDCl_3$) δ 14.47 (CH_3), 23.61 (CH_2), 155.35 (C=). Anal. Calcd for $C_{12}H_{20}Cl_4Si_2$: C, 39.78; H, 5.56. Found: C, 39.85; H, 5.59. For data of other minor products and the X-ray structure of compound **3**, see the Supporting Information. The Cambridge Crystallographic Data Base file CCDC 200443 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, U.K., fax (+44) 1223-336-033, e-mail deposit@ccdc.cam.ac.uk).