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Platinum-catalyzed double silylations of alkynes with bis(dichlorosilyl)methanes

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Abstract

Bis(dichlorosilyl)methanes **1** undergo the two kind reactions of a double hydrosilylation and a dehydrogenative double silylation with alkynes **2** such as acetylene and activated phenyl-substituted acetylenes in the presence of Speier's catalyst to give 1,1,3,3-tetrachloro-1,3-disilacyclopentanes **3** and 1,1,3,3-tetrachloro-1,3-disilacyclopent-4-enes **4** as cyclic products, respectively, depending upon the molecular structures of both bis(dichlorosilyl)methanes (**1**) and alkynes (**2**). Simple bis(dichlorosilyl)methane (**1a**) reacted with alkynes [R^1–C≡C–R^2: R^1 = H, R^2 = H (**2a**), Ph (**2b**); R^1 = R^2 = Ph (**2c**)] at 80 °C to afford 1,1,3,3-tetrachloro-1,3-disilacyclopentanes **3** as the double hydrosilylation products in fair to good yields (33–84%). Among these reactions, the reaction with **2c** gave a *trans*-4,5-diphenyl-1,1,3,3-tetrachloro-1,3-disilacyclopentane **3ac** in the highest yield (84%). When a variety of bis(dichlorosilyl)(silyl)methanes [(Me_n-Cl_{3-n}Si)CH(SiHCl_2)_2$: n = 0 (**1b**), 1 (**1c**), 2 (**1d**), 3 (**1e**)] were applied in the reaction with alkyne (**2c**) under the same reaction conditions. The double hydrosilylation products, 2-silyl-1,1,3,3-tetrachloro-1,3-disilacyclopentanes (**3**), were obtained in fair to excellent yields (38–98%). The yields of compound **3** deceased as follows: n = 1 > 2 > 3 > 0. The reaction of alkynes (**2a**–**c**) with **1c** under the same conditions gave one of two type products of 1,1,3,3-tetrachloro-1,3-disilacyclopentanes **3** and 1,1,3,3-tetrachloro-1,3-disilacyclopent-4-enes (**4**): simple alkyne **2a** and terminal **2b** gave the latter products **4ca** and **4cb** in 91% and 57% yields, respectively, while internal alkyne **2c** afforded the former cyclic products **3cc** with *trans* form between two phenyl groups at the 3- and 4-carbon atoms in 98% yield, respectively. Among platinum compounds such as Speier's catalyst, $PtCl_2(PEt_3)_2$, $Pt(PPh_3)_2(C_2H_4)$, $Pt(PPh_3)_4$, Pt[ViMeSiO]_4$, and Pt/C, Speier's catalyst was the best catalyst for such silylation reactions.
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1. Introduction

Si–C bond forming reactions such as the direct reaction [1–4] and general organometallic reactions [5–7] are important methods for the preparation of various organosilicon compounds. Another established Si–C bond forming reaction is the addition of silanes containing Si–H bond(s) to unsaturated organic compounds, commonly known as the hydrosilylation reaction [8–10]. This reaction became one of the most effective and elegant method for synthesizing

the organosilicon and related compounds, since it was discovered by J.L. Speier in 1957 [11] that a hexachloroplatinic acid in *i*-propyl alcohol (Speier's catalyst) was a very effective catalyst for hydrosilylation [12].

Recently, we have developed the direct synthesis of organochlorosilanes having Si–C–Si linkages [13] by the reaction of elemental silicon with the mixture of excess hydrogen chloride and (dichloromethyl)silanes [14], methylene chloride [15], and chloroform [16]. From these reactions, novel bis(dichlorosilyl)methane derivatives were successfully prepared and applied in the hydrosilylation of unsaturated hydrocarbons in the presence of palladium catalyst [17]. When the bis(dichlorosilyl)methane derivatives
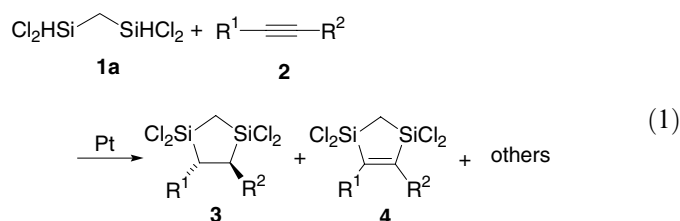
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was reacted with alkynes in the presence of palladium catalyst, 1,3-disilacyclopent-4-enes were surprisingly obtained in good yields through the dehydrogenative double silylation reaction [18]. In a series, the same reactions were carried out in the presence of other group 10 metal compounds. When Speier's catalyst was used, two kind reactions of the double hydrosilylation and dehydrogenative double silylation occurred to give 1,1,3,3-tetrachloro-1,3-disilacyclopentanes and 1,1,3,3-tetrachloro-1,3-disilacyclopent-4-enes, respectively, depending upon the molecular structures of both alkynes and silanes. Herein, we wish to report the two type silylation reactions of alkynes 2 with bis(dichlorosilyl)methanes 1 in the presence of Speier's catalyst in details.

2. Results and discussion

2.1. Hydrosilylation reaction of bis(dichlorosilyl)methane with alkynes

Simple bis(dichlorosilyl)methane (1a) reacted with alkynes 2 [R^1–C≡C–R^2: R^1 = H, R^2 = H (a), Ph (b); R^1 = R^2 = Ph (c)] in the presence of Speier's catalyst to give 1,1,3,3-tetrachloro-1,3-disilacyclopentanes 3a–c as major cyclic products (Eq. (1)). The results are summarized in Table 1.

$$\text{Cl}_2\text{HSi}\diagup\diagdown\text{SiHCl}_2 + R^1\text{———}R^2$$

1a   **2**

$$\xrightarrow{\text{Pt}} \begin{array}{c}\text{Cl}_2\text{Si}\diagdown\diagup\text{SiCl}_2\\ \diagup\quad\diagdown\\ R^1\qquad R^2\\ \textbf{3}\end{array} + \begin{array}{c}\text{Cl}_2\text{Si}\diagdown\diagup\text{SiCl}_2\\ \diagup\quad\diagdown\\ R^1\qquad R^2\\ \textbf{4}\end{array} + \text{others} \qquad (1)$$

As shown in Table 1, the reaction of alkynes 2a–c with 1a gave the double hydrosilylation compounds 3 as the major cyclic products in fair to good yields (33–84%). The reactivity of alkynes increases as the number of alkyl substituent(s) on carbon–carbon with a triple bond increase. When a simple acetylene (2a) was bubbled into a stirring solution of 1a and Speier's catalyst in toluene at 80 °C for 3 h, two cyclic compounds, 1,1,3,3-tetrachloro-1,3-disilacyclopentane (3aa) and 1,1,3,3-tetra-

chloro-1,3-disilacyclopent-4-ene (4aa) [17], were obtained in 45% and 4% yields, respectively, from a 96% consumption of 1a. Compounds 3aa and 4aa were produced by double hydrosilylation and dehydrogenative double silylation reactions, respectively. In the cases of phenyl-substituted acetylenes, a 94% of a phenyl-substituted acetylene 2b for 2 h at 80 °C was consumed to give only 4-phenyl-1,1,3,3-tetrachloro-1,3-disilacyclopentane (3ab, 33%) [17] as the double hydrosilylation cyclic product, while the reaction of diphenyl-substituted acetylene 2c was completed within 1 h at 80 °C to give trans-4,5-diphenyl-1,1,3,3-tetrachloro-1,3-disilacyclopentane (3ac) in the highest 84% yields. The results suggest that the reaction of inner alkynes is faster than that of terminal alkyne or simple acetylene for the formation of the double hydrosilylation product 3 and the yield of compound 3 is the best from the reaction of alkyne (2c) among alkynes 2a–c. In contrast to this Pt-catalyzed reaction with 1a, palladium-catalyzed reaction afford the dehydrogenative double silylation products, 1,1,3,3-tetrachloro-1,3-disilacyclopent-4-enes (4) previously reported [17]. It is at this time difficult to explain the difference of catalysis patterns between platinum and palladium compounds in the reaction of alkynes with bis(dichlorosilyl)methane. In the reaction of 3-hexyne (2d) as aliphatic inner alkene was completed within 30 min to give the double hydrosilylation cyclic product, 4-(n-propyl)-1,1,3,3-tetrachloro-1,3-disilacyclohexane (3ad′), as the major product in 63% yield, but no 1,3-disilacyclopentane 3ad. The six-membered ring compound 3ad′ could be produced by the terminal-migration and hydrosilyation of carbon–carbon double bond on silylated hexane formed from a hydrosilylation of alkyne 2d. This may be regarded as analogous to the formation of terminal adducts in the chloroplatinic acid catalyzed hydrosilylation of internal aliphatic olefins which has been observed by several workers [19]. The configuration of compound 3ac was characterized by the analyses of ^{1}H NMR data. ^{1}H NMR data of 3ac showed two resonance signals with singlets at 1.64 ppm and at 3.62 ppm for two protons of a methylene and for two benzylic protons in the aliphatic region, indicating trans-form between two phenyl-substituents on the five-membered-ring in which two protons of methylene and of two benzylic-protons are the chemically equivalent environmental condition, respectively.

2.2. Hydrosilylation reaction of alkyne (2c) with bis(dichlorosilyl)(silyl)methanes

Bis(dichlorosilyl)(silyl)methanes [$Me_nCl_{3-n}Si]CH(SiHCl_2)_2$:n = 0 (1b), 1 (1c), 2 (1d), 3 (1e)] in place of simple 1a were employed in this reaction. On the basis of the results obtained from the reaction of alkynes 2a–c with 1a, alkyne (2c) was used as a representative among alkynes 2a–d for the reaction with bis(dichlorosilyl)(silyl)methanes (1b–e). Reaction of 2c with 1b–e in the presence of Speier's catalyst at 80 °C gave only trans-4,5-diphenyl-2-silyl-1,1,3,3-tetrachloro-1,3-disilacyclopentanes 3 as the double silylation

Table 1
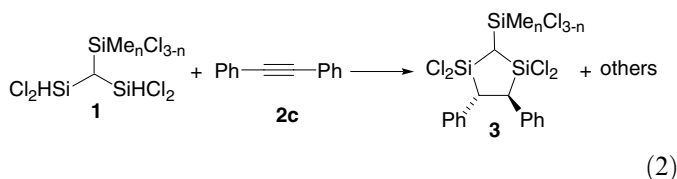Silylation reaction of alkynes with 1a in the presence of Speier's catalyst[a]

1a[b]	2			Reaction time (h)	Product cyclic yields (%)[b]	
		R^1	R^2		3	4
4	2a	H	H	3	3aa, 45	4aa, 4
6	2b	Ph	H	2	3ab, 33	Trace
–	2c	Ph	Ph	1	3ac, 84[c]	–

[a] 1:1 Reactions of 1a with alkynes 2 using 0.5 mol% Pt compound (based on 1a used) were carried out at 80 °C in toluene solvent.
[b] Unreacted 1a (%) and yields (based on 1a used) were determined by GLC using n-dodecane as an internal standard.
[c] Isolated yields.

products (Eq. (2)). The dehydrogenative double silylation products **4** could not be obtained in appreciable amounts. The results are summarized in Table 2.

$$Cl_2HSi-\underset{SiHCl_2}{\overset{SiMe_nCl_{3-n}}{\mathsf{CH}}} \quad + \quad Ph \!=\!\!=\! Ph \quad \longrightarrow \quad Cl_2Si \overset{SiMe_nCl_{3-n}}{\underset{Ph\quad Ph}{\bigcirc}} SiCl_2 \quad + \text{ others}$$

$$\text{(2)}$$

As shown in Table 2, the yields of cyclic products **3** formed by the double hydrosilylation vary greatly depending upon the substituents on the silyl of bis(dichlorosilyl)(silyl)methanes **1**. Trichlorosilyl-substituted bis(dichlorosilyl)methane (**1b**) reacted with alkyne **2c** to give the double hydrosilylation product **3bc** in low yield (38%). While the reactions of other bis(dichlorosilyl)(silyl)methanes containing one more methyl substituent(s) **1c–e** gave the double hydrosilylation products **3cc** (98%), **3dc** (92%), and **3ec** (81%) in good to excellent yields, respectively. Although none of the starting materials was recovered after the reaction of **1b**, the yield of **3bc** was only 38% and the balance was polymeric materials which were formed by the intermolecular hydrosilylation reaction with **2c**. The yield of double hydrosilylation product increases as the number of Cl group(s) ($n = 1$–3) on the silyl of bis(dichlorosilyl)(silyl)methanes **1** increases as follows: $SiMeCl_2 > SiMe_2Cl > SiMe_3$. While the reactivity of **1b** containing a trichlorosilyl substituent was the fastest one among reactants **1b–e**. Compounds **3bc–3ec** were characterized by the analyses of ^{1}H NMR data. Their proton NMR data showed two resonance signals with doublets ($J = 16$ Hz) for two benzylic protons around 3.5 ppm of the aliphatic region. In the case of **3cc**, a single crystal of **3cc** for an X-ray diffraction study was successfully grown as a colorless from a concentrated hexane solution. The ORTEP plot and the bond lengths and angles of compound **3cc** are depicted in Fig. 1. In Fig. 1, the structure of **3cc** was disclosed to be a five-membered-ring compound with *trans* form between two phenyl-substituents. The torsion angle of C5–C2–C3–C11 is −63.4°.

2.3. Reactions of alkynes *2a–c* with *1c*

Reaction of bis(dichlorosilyl)methane (**1c**) with alkynes **2a–c** in the presence of Speier's catalyst was carried out
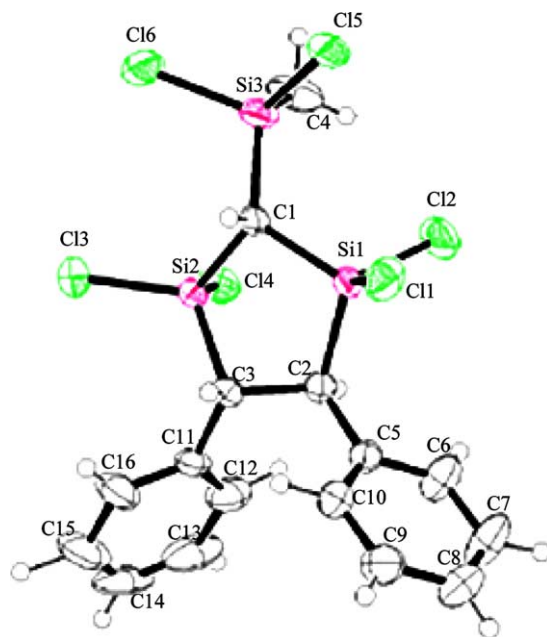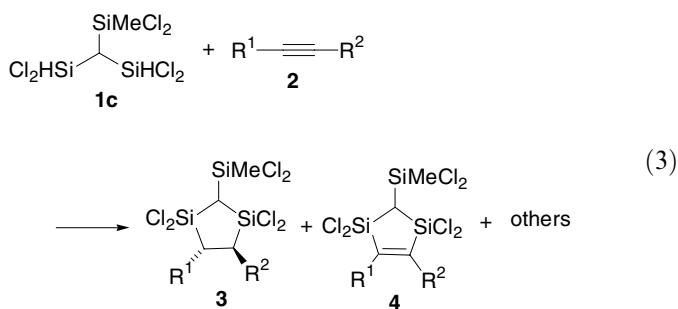

Fig. 1. The ORTEP plot of **3cc** (carbon: black, silicon: pink, chlorine: green colors). Selected bond lengths (Å) and angles (deg): Si(1)–C(1) 1.875(3), Si(1)–C(2) 1.889(3), Si(2)–C(1) 1.863(3), Si(2)–C(3) 1.873(3), Si(3)–C(1) 1.846(3), Si(3)–C(4) 1.830(4), C(2)–C(3) 1.555(4), C(2)–C(5) 1.522(4), C(3)–C(11) 1.517(4); C(1)–Si(1)–C(2) 104.68(12), C(1)–Si(2)–C(3) 101.15(12), C(4)–Si(3)–C(1) 118.34(15), Si(3)–C(1)–Si(2) 121.53(15), C(5)–C(2)–C(3) 115.6(2), C(5)–C(2)–Si(1) 113.52(19), C(3)–C(2)–Si(1) 106.45(17), C(11)–C(3)–C(2) 116.20(2), C(11)–C(3)–Si(2) 114.32(19), C(2)–C(3)–Si(2) 105.33(18). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

at 80 °C in toluene solvent. In these reactions, both type products of double hydrosilylation and dehydrogenative double silylation were obtained (Eq. (3)). The results are summarized in Table 4.

$$Cl_2HSi-\underset{SiHCl_2}{\overset{SiMeCl_2}{\mathsf{CH}}} \quad + \quad R^1 \!=\!\!=\! R^2$$
$$\mathbf{1c} \qquad\qquad\qquad \mathbf{2}$$

$$\longrightarrow \quad Cl_2Si\overset{SiMeCl_2}{\underset{R^1\quad R^2}{\bigcirc}}SiCl_2 \;+\; Cl_2Si\overset{SiMeCl_2}{\underset{R^1\quad R^2}{\bigcirc}}SiCl_2 \;+\; \text{others}$$
$$\qquad\qquad \mathbf{3} \qquad\qquad\qquad \mathbf{4}$$

$$\text{(3)}$$

As shown in Table 3, when **1c** reacted with simple alkyne **2a** for 10 h and terminal **2b** for 2 h at 80 °C, respectively, dehydrogenative double silylation products **4ca** and **4cb** [17] were obtained as major products in 91% and 57% yields [17] (on the basis of **1c** used) from a 93% and a 89% consumption of **1c**, respectively. While the reactions with internal alkyne **2c** afforded predominantly 1,3-disila-4,5-diphenylcyclopentanes (**3cc**) in 98% yield. These results indicate that silylation type of alkyne with **1c** in the presence of Speier's catalyst vary greatly, depending on the molecular structure of alkyne: simple alkynes **2a** and **2b** give the dehydrogenative double silylation products, which

Table 2
Hydrosilylation reaction of **2c** with **1b–e** using Speier's catalyst

Reactant		Time (h)[a]	**3** (%)[b]
1	*n*		
1b	0	1.5	**3bc**, 38[c]
1c	1	2	**3cc**, 98
1d	2	2	**3dc**, 92
1e	3	2	**3ec**, 81

[a] 1:1 Reactions of **2c** with compounds **1a–e** using 0.5 mol% Pt compound were carried out at 80 °C using toluene solvent.
[b] Isolated yields.
[c] Polymeric materials were obtained.

Table 3
Reactions of **1c** with alkynes **2a–d** in the presence of Speier's catalyst[a]

Reactant			Reaction time (h)	Unreacted 1c (%)[b]	Product yields (%)[c]	
	R^1	R^2			3	4
2a	H	H	10	7	–	**4ca**, 91
2b	H	Ph	2	11	**3cb**, Trace[d]	**4cb**, 57
2c	Ph	Ph	2	Trace	**3cc**, 98	–

[a] 1:1 Reactions of compounds **2a–d** with **1c** using 0.5 mol% Pt compound were carried out at 80 °C in toluene solvent.
[b] Unreacted **1c** was determined by GLC using *n*-dodecane as an internal standard.
[c] Isolated yield.
[d] **3cb** was detected as a trace by GC/MS.

are the same products obtained from the reactions in the presence of Pd[PPh₄]₄ catalyst [17], but internal alkyne **2c** afforded double hydrosilylation product as new type compound.

2.4. Catalytic activity of group 10 transition metal compounds for the reaction of alkyne (2c) with 1c

The reaction of alkyne **2c** with 1,3-bis(dichlorosilyl)methane **1c** was carried out in toluene using various group 10 transition metal complexes as catalysts (Eq. (4)). The results are summarized in Table 4.
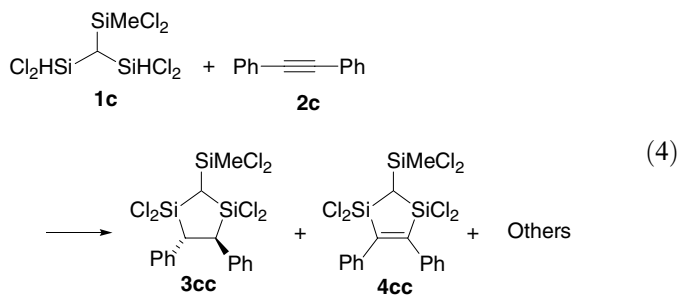
Table 4
Catalytic effect of group 10 transition metal compounds in the double silylation of **1c** with **2c**

Reaction conditions[a]		Unreacted 1c (%)[c]	Products (%)[c]	
Catalyst	Time (h)		3cc	4cc
Speier's catalyst[b]	2	–	98[d]	–
Pt[ViMeSiO]₄	10	44	15	Trace
PtCl₂(PEt₃)₂	10	15	2	1
Pt(PPh₃)₂(C₂H₄)	10	–	10	8
Pt(PPh₃)₄	10	50	–	–
Pt/C	10	98	–	–
Pd[PPh₃]₄	15	48	–	5
PdCl₂	15	–	–	–
Ni[PPh₃]₄	15	66	–	Trace
NiCl₂	15	–	–	–

[a] 1:1 Reactions of **1c** with **2c** using 0.5 mol% transition metalcompounds were carried out under the reflux temperature of toluene.
[b] Reaction temperature was 80 °C.
[c] Unreacted **1c** and yields (based on **1c** used) were determined by GLC using *n*-dodecane as an internal standard.
[d] Isolated yield.

As shown in Table 4, the reaction using Speier's catalyst gave *trans*-4,5-diphenyl-1,3-disilacyclopentane (**3cc**) in a quantitative yield at 80 °C for 2 h. When Pt[ViMeSiO]₄ was used as catalyst, 56% consumption of **1c** at the reflux temperature of toluene for 10 h gave **3cc** (15%) and polymeric materials but the dehydrogenative double silylation product **4cc** [17] was not detected. The reaction using Pt(PPh₃)₂(C₂H₄) afforded **3cc** (10%) and 4,5-diphenyl-1,3-disilacyclopent-4-ene (**4cc**) (8%) as a dehydrogenative double silylation product, and polymeric materials at the reflux temperature of toluene for 10 h. However, the other platinum compounds such as PtCl₂(PEt₃)₂, Pt(PPh₃)₄, and Pt/C are almost ineffective for this reaction. Although tetrakis(triphenyl-phosphine)palladium Pd[PPh₃]₄, was a good catalyst for the dehydrogenative double silylation reactions [17], the reaction of **1c** with **2c** gave only **4cc** in low 5% yield and the double hydrosilylation product **3cc** was not detected. The reaction using other group 10 metal compounds PdCl₂, NiCl₂, and Ni[PPh₃]₄ did not give cyclic silylation product. In this study, it was found that Speier's catalyst was the best catalyst for double hydrosilylation reaction. The active species of Speier's catalyst for hydrosilylation was well-described in the literature [12b]. These results give some important information on the relationship between the structures of the catalysts and the products.

2.5. Mechanism

On the basis of our results and previous reports [17,18], a plausible catalytic mechanism is proposed in Scheme 1, which accommodates two pathways to afford the intramolecular double hydrosilylation and dehydrogenative double silylation products in the presence of Speier's catalyst. For the double hydrosilylation reaction to compound **3**, an oxidative addition of the Si–H bond of **1c** to platinum presumably occurs first to generate intermediate **I**. The intermediate **I** interacts with alkyne to give an intermediate **II** and then the alkyne is inserted into the Pt–H or the Pt–Si bond leading to an intermediate **IIIa** or **IIIb**. The intermediate **IIIa** is (i) reductive elimination of H and C atom to form Pt(0) and (ii) oxidative addition of another Si–H bond to Pt(0) to form an intermediate **IV**. Another possible reaction pathway to **IV** from **II** is (i) the intramolecular insertion of a [Pt] atom on **IIIb** into the second Si–H bond and (ii) the reductive elimination of a hydrogen and a carbon atom on [Pt] to form the intermediate **IV**. Subsequently, a hydrogen and silicon atom on platinum of the intermediate **IV** add intramolecularly to a carbon–carbon double bond coincided with liberating platinum to give compound **3cc**. It was reported by Sakaki et al. that the insertion of ethene into the Pt–H bond is much easier than that into the Pt–Si-bond from the theoretical calculations for the reaction with Pt(SiH₃)(H)(PH₃)₂ [20]. On this result, it seems likely that the formation of intermediate **IIIa** is favorable to that of the intermediate **IIIb**. For other pathway to compound **4**, the platinum of intermediate **I** adds intramolecularly to the second Si–H and a dihydrogen is
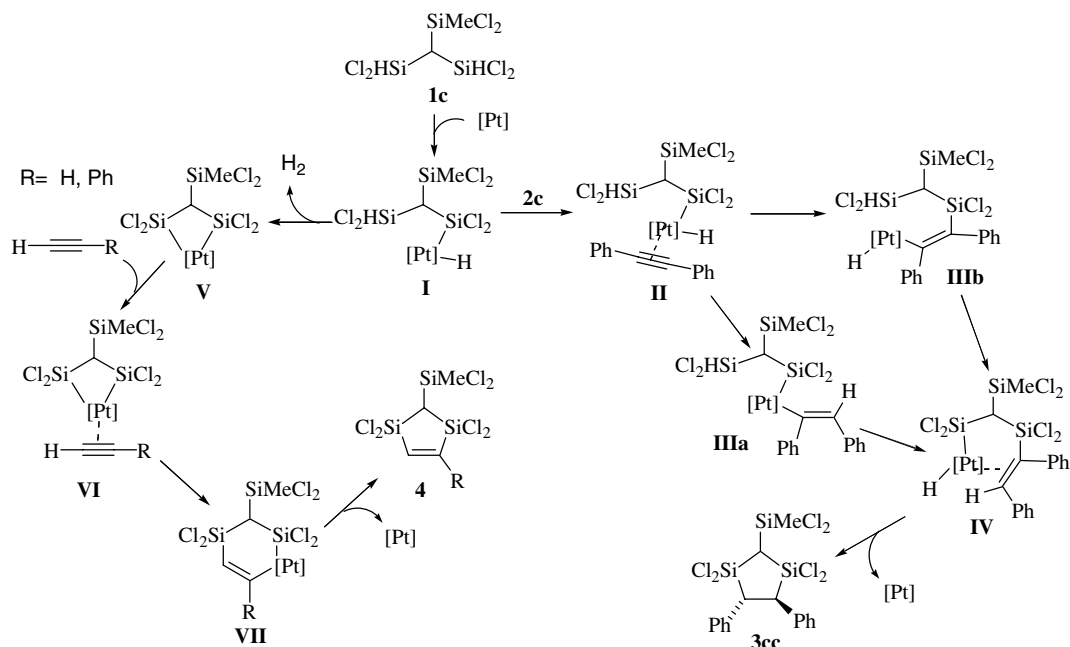
Scheme 1. Proposed mechanism for the double hydorsilylation and dehydrogenative double silylation of alkynes with **1c** in the presence of Speier's catalyst.

librated to form a intermediate **V**, then coordinating to alkyne to generate an intermediate **VI**. Then alkyne at the intermediate **VI** is intramolecularly inserted to Pt–Si bond to form an intermediate **VII**. Finally, a carbon and silicon atom on platinum of the intermediate **VII** couple to form a carbon–silicon bond coincided with liberating platinum to give compound **4**.

In conclusion, bis(dichlorosilyl)methanes **1** underwent two type double silylations of double hydrosilylation reaction and the dehydrogenative double silylation with alkynes **2** in the presence of Speier's catalyst to give the cyclic products, 1,1,3,3-tetrachloro-1,3-disilacyclopentanes **3** and 1,1,3,3-tetrachloro-1,3-disilacyclopent-4-enes **4**, upon the molecular structures of both reactants **1** and **2**. The reaction with simple bis(dichlorosilyl)methane (**1a**) afforded 1,1,3,3-tetrachloro-1,3-disilacyclopentanes as the double hydrosilylation products. The reaction with bis(dichlorosilyl)-(silyl)methane **1c** under the same conditions gave two type products of 1,1,3,3-tetrachloro-1,3-disilacyclopentanes **3** or 1,1,3,3-tetrachloro-1,3-disilacyclopent-4-enes **4**: simple alkyne **2a** and terminal **2b** gave the latter cyclic products **4a** and **4b** as major products, respectively, while internal alkyne **2c** afforded the former cyclic product **3c** with *trans* form between two phenyl groups at the 3,4-carbon atoms as major products, respectively.

3. Experimental

3.1. General comments

All reactions and manipulations were carried out with flame-dried glassware under nitrogen. All air sensitive liquids were transferred by standard syringe or double tipped

needle techniques. All starting silane compounds such as bis(dichlorosilyl)methane and bis(dichlorosilyl)(silyl)methanes were prepared through the modified direct synthesis method previously described [13–15]. Acetylene gas was commercially available and purified by passing it through a dry ice-acetone trap and then a calcium chloride drying tube. Solvents were dried according to standard procedures [21]. All other chemicals were purchased from Aldrich Chemical Co. and used as received unless otherwise noted. The progresses of reaction were monitored and product yields were determined by GLC using a packed column (10% OV-101 on 80–100 mesh Chromosorb W/AW, 1/8 in. × 1.5 m) or a capillary column (HP-1, 0.11 μm, ID 0.2 mm × 25 m) with a Varian 3300 gas chromatograph equipped with a thermal conductivity detector unless otherwise noted. NMR spectra were recorded on a Bruker Avance 300 spectrometer (300 MHz for ^{1}H; 75 MHz for ^{13}C) using CDCl$_3$ as a solvent. The chemical shifts are given in ppm relative to the residual proton signal of the solvent: CDCl$_3$ 7.25 ppm (1H) and 77.0 ppm (13C). Melting points (uncorrected) were measured with a Mel-Temp II melting point apparatus using sealed capillary tubes. GC–MS data were obtained with a HP6890/5973 system (70 eV, EI). Elemental analyses were performed by the Advanced Analysis Center of the Korea Institute of Science and Technology.

3.2. General procedure for the double hydrosilylation of acetylene (2a) with 1a

Into a 100 mL, two necked, flame dried, round bottom flask equipped with a magnetic stirrer, 0.75 mL of 0.1 M H$_2$PtCl$_6$ in isopropyl alcohol was placed under dry

nitrogen atmospheric pressure. After removed isopropyl alcohol under vacuum from the flask, 3.21 g (15.0 mmol) of **1a** and 75 mL of dried toluene were added. The reaction mixture was wormed up to 80 °C. Then, acetylene (**2a**) gas through gas inlet adapter was blown into the stirring solution of reaction mixture at a rate of 50 mL/min for 10 h. The reaction products were vacuum distilled at 0.5 torr to give 1.62 g of **3aa** [17,22,23] in 45% yield. The mixture of high boilers (1.95 g) remained in flask was very messy in NMR spectra.

The reactions of **1a** (3.21 g, 15.0 mmol) with other alkynes **2b–d** (15.0 mmol) were carried out under the same reaction conditions except for adding other alkynes dissolved in toluene (15 mL) to the flask for 1 h. The results obtained from the reaction of **1a** with **2b–c** are summarized in Table 1. The reaction mixture obtained from the reaction of **2d** with **1a** was vacuum-distilled to give 4-(n-propyl)-1,1,3,3-tetrachloro-1,3-disilacyclohexane (2.8 g, **3ad′**) in 63% isolated yield. The mixture of high boilers obtained from each reaction was very messy in NMR spectra.

To a stirring solution of compound **3ad′** (0.23 g, 0.78 mmol) in 10 mL THF was added dropwise 3 M methyl magnesium bromide in THF (1.2 mL, 3.58 mmol) for 5 min. Then the reaction mixture was refluxed for 30 min and treated with 10 mL of a saturated aqueous ammonium chloride. The organic layer was separated and combined with three hexane extraction of the aqueous layer, and dried with anhydrous magnesium sulfate. 4-(n-Propyl)-1,1,3,3-tetramethyl-1,3-disilacyclohexane (**5ad**, 0.14 g) was obtained in 84% yield and purified by a preparative GLC.

Data for **3ac**: white solid; m.p. 155–157 °C; ^{1}H NMR δ 1.64 (s, 2H, SiCH_2Si), 3.62 (s, 2H, CHPh), 7.27–7.41 (m, 10H, ArH); ^{13}C NMR δ 11.37 (1C, SiCH$_2$Si), 40.46 (2C, CH–CH), 126.25, 127.57, 128.49, 134.67 (12C, ArC). Anal. calc. for $C_{15}H_{14}Cl_4Si_2$: C, 45.93; H, 3.60. Found: C. 46.23; H, 3.76%. Data for **3ad′**: colorless liquid; b.p. 44–46 °C/0.5 torr; ^{1}H NMR δ 0.92 (t, 6H, CH_3. $J = 6.97$ Hz), 1.05–1.19 (m, 2H, SiCH_2Si), 1.29–1.82 (m, 4H, CHCH_2), 2.09–2.31 (m, 2H, CHCH_2); ^{13}C NMR δ 13.90 (1C, SiCH$_2$Si), 16.39, 21.77 (2C, CH$_2$CH$_3$), 20.50, 21.11 (2C, CH$_3$), 30.33, 31.60 (2C, CHCH$_2$). Anal. calc. for $C_7H_{14}Cl_4Si_2$: C, 28.39; H, 4.76. Found C, 28. 54; H, 4.88%. Data for **5ad**: ^{1}H NMR (CDCl$_3$) δ −0.38 (d, $J_{gem} = 14$ Hz, 1H), −0.24 (dd, $^2J_{gem} = 14$ Hz, $^4J_{HC–Si–CH} = 1.5$ Hz, 1H) (SiCH_2Si), −0.04, −0.01, −0.006, −0.011 (s, 3H, SiCH_3), 0.33–0.50 (m, 1H), 0.63–0.72 (m, 1H) (SiCH_2), 0.33–0.50 (m, 1H, SiCH), 0.86 (t, 7.2 Hz, 3H, CH_3CH$_2$), 1.05–1.26 (m, 1H), 1.27–1.53 (m, 1H) (CH$_3$CH_2), 1.05–1.26 (m, 1H), 1.27–1.53 (m, 1H) (CH$_3$CH$_2$CH_2), 1.27–1.53 (m, 1H), 1.85–1.94 (m, 1H) (SiCH$_2$CH_2CH); ^{13}C NMR (CDCl$_3$) δ −3.4, −0.9, 0.0, 0.8 (SiCH$_3$), 0.7 (SiCH$_2$Si), 14.3 (CH$_2$CH$_3$), 15.4 (SiCH$_2$CH$_2$CH), 21.8 (CH$_2$CH$_3$), 24.6 (SiCH$_2$$CH_2$CH), 27.1 (Si$CHCH_2$), 32.6 ($CH_2CH_2CH_3$). MS (70 eV, EI) m/z (relative intensity): 214 (3, M+), 133 (10), 132 (19), 131 (100), 129 (20), 117 (15), 73 (20), 59 (14).

3.3. General procedure for the double hydrosilylation of alkyne **2a** with **1c**

Into a 100 mL, two necked, flame dried, round bottom flask equipped with a magnetic stirrer, 0.75 mL of H$_2$PtCl$_6$ (0.1 M in isopropyl alcohol) was placed under dry nitrogen atmospheric pressure. After removed isopropyl alcohol under vacuum, 4.91 g (15.0 mmol) of **1c** and 75 mL of dried toluene were added. The acetylene gas through gas inlet adapter was blown into the solution at a rate of 50 mL/min for 10 h. The temperature was maintained at 80 °C. The reaction products were vacuum distillated at 0.5 torr to give 4.80 g of **4ca** [17] in 91% yield.

The reactions of **1c** (4.91 g, 15.0 mmol) with other alkynes **2b–c** (15.0 mmol) were carried out under the same reaction conditions except for adding other alkynes dissolved in toluene (15 mL) to the flask for 1 h. The results are summarized in Table 3.

3.4. Reaction of alkyne **2c** with bis(dichlorosilyl)methane **1c**

Into a 100 mL, two necked, flame dried, round bottom flask equipped with a magnetic stirrer, 0.75 mL of H$_2$PtCl$_6$ (0.1 M in isopropyl alcohol) was placed under dry nitrogen atmospheric pressure. After removed isopropyl alcohol under vacuum from the flask, **1c** (4.91 g, 15 mmol) and 60 mL of dried toluene were added. After mixed over 10 min, **2c** (2.67 g, 15.0 mmol) dissolved in 15 mL of dried toluene was added dropwise into the reaction mixture for 1 h at 70 °C. The reaction mixture was then maintained at 80 °C for another 1 h. The reaction products were vacuum distilled at 0.5 torr to give 7.39 g of 2-methyl-dichlorosilyl-1,1,3,3-tetrachloro-4,5-diphenyl-1,3-disilacyclopentane (**3cc**) in 98% yield. The similar reactions of alkyne **2c** with other bis(dichlorosilyl)(silyl)methanes **1b,d,e** were carried out under the same reaction condition above. The results are summarized in Table 2. Single crystal of **3cc** for X-ray crystallographic determination was grown from a concentrated hexane solution. Data for **3bc**: white solid; m.p. 130–132 °C; ^{1}H NMR δ 1.92 (s, 1H, SiCHSi), 3.43 (d, 1H, $J = 16$ Hz), 3.51 (d, 1H, $J = 16$ Hz) (CHPh), 7.12–7.23 (m, 10H, ArH); ^{13}C NMR δ 24.33 (SiCHSi), 39.85, 40.02 (Ph–CH), 126.69, 127.71, 127.75, 128.67, 133.17, 133.49 (ArC). Anal. calc. for $C_{15}H_{13}Cl_7Si_3$: C, 34.27; H, 2.49. Found: C, 34.39; H, 2.55%. Data for **3cc**: white solid, m.p. 137–139 °C; ^{1}H NMR, δ: 1.12 (s, 3H, SiCH_3), 1.71 (s, 1H, SiCHSi), 3.45 (d, 1H, $J = 16$ Hz), 3.52 (d, 1H, $J = 16$ Hz) (CHPh), 7.12–7.2.7 (m, 10H, ArH); ^{13}C NMR, δ: 8.17 (SiCH$_3$), 22.02 (SiCHSi), 40.24, 40.31 (Ph–CH), 126.55, 127.68, 128.61, 133.56, 133.96 (ArC). Anal. calc. for $C_{16}H_{16}Cl_6Si_3$: C, 38.03; H, 3.19. Found: C. 38.25; H, 3.22%. Data for **3dc**: white solid; m.p. 106–108 °C; ^{1}H NMR (CDCl$_3$, ppm) 0.91 (s, 6H, SiCH_3), 1.50 (s, 1H, SiCHSi), 3.56 (d, 1H, $J = 16$ Hz), 3.63 (d, 1H, $J = 16$ Hz) (CHPh), 7.27–7.40 (m, 10H, ArH); ^{13}C NMR (CDCl$_3$, ppm): 4.71 (SiCHSi), 19.06

(SiCH_3), 40.56, 40.61 (Si$CHCH$Si), 126.37, 127.65, 127.67, 128.51, 128.55, 134.10, 134.50 (12C, ArC). Anal. calc. for $C_{17}H_{19}Cl_5Si_3$: C, 42.11; H, 3.95. Found: C, 42.34; H, 4.02%. Data for **3ec**: white solid; m.p. 126–128 °C; ^{1}H NMR δ 0.36 (s, 9H, CH_3Si), 0.90 (s, 1H, SiCHSi), 3.38 (d, 1H, $J = 16$ Hz), 3.44 (d, 1H, $J = 16$ Hz) (CHPh), 7.08–7.24 (m, 10H, ArH); ^{13}C NMR δ 1.27 (CH$_3$Si), 15.85 (SiCHSi), 40.81, 41.04 (Ph–CH), 126.15, 127.64, 128.39, 134.77, 135.12 (m, 12C, ArC). Anal. calc. for $C_{18}H_{22}Cl_4Si_3$: C, 46.55; H, 4.77. Found: C, 46.35; H, 4.79%.

3.5. Catalytic activity of group 10 metal compounds for the reaction of alkyne 2c with 1c

Using the same molar scale and procedure above, the catalytic effects of a variety of group 10 metal compounds such as Speier' catalyst, Pt[ViMe$_2$SiO]$_4$, Pt(C$_2$H$_4$)(PPh$_3$)$_2$, PtCl$_2$(PEt$_3$)$_2$, Pt(PPh$_3$)$_4$, Pt/C, Pd(PPh$_3$)$_4$, PdCl$_2$, NiCl$_2$, and Ni(PPh$_3$)$_4$ were studied. Reactions using NiCl$_2$ and PdCl$_2$ afforded some bis(trichlorosilyl)methane, methyltrichlorosilane, and polymeric materials. Polymeric materials were very messy in NMR spectra. These results are summarized in Table 3.

3.6. X-ray crystallography

All X-ray data were collected on a Siemens SMART CCD area detector with graphite monochromated Mo K radiation (0.71073 Å) source at ambient temperature. Unit cell dimensions were based on 25 well-centered reflections by using a least-squares procedure. During the data collection, three standard reflections monitored after every hour did not reveal any systematic variation in intensity. The structures were solved by the SHELXS-97 [24], followed by successive difference Fourier synthesis. The non-hydrogen atoms were refined anisotropically and hydrogen atoms were placed in calculated positions and refined only for the isotropic thermal factors. All calculations were carried out on a personal computer with use of SHELXS-97 and SHELXL-97. Crystal data of **3cc** are as followings: $C_{16}H_{16}Cl_6Si_3$ (fw = 505.26), monoclinic, $a = 10.747(3)$ Å [$\alpha = 90°$], $b = 8.712(2)$ Å [$\beta = 97.304(4)°$], $c = 24.076(6)$ Å [$\gamma = 90°$], $V = 2235.9(9)$ Å^3, $\lambda = 0.71073$ Å, $\mu = 0.929$ mm^{-1}, $Z = 2$, $d_{calcd.} = 1.501$ g cm^{-3}, R_1(all data) = 0.0581, $wR_2 = 0.1378$.

4. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. CCDC 257340 for compounds **3cc**. Copies of this information may be obtained free of charge from the Director, CCDC, 12 Union Road Cambridge, CB2 1EZ, UK (fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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