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SYNTHESIS OF 1,1-DICHLORO-2,5-DIPHENYLSILACYCLOPENT-3-ENES BY THE CHLORINATION OF 1,1-DIETHOXY- AND BIS(OPTICALLY ACTIVE ALKOXY)-2,5-DIPHENYLSILACYCLOPENT-3-ENES

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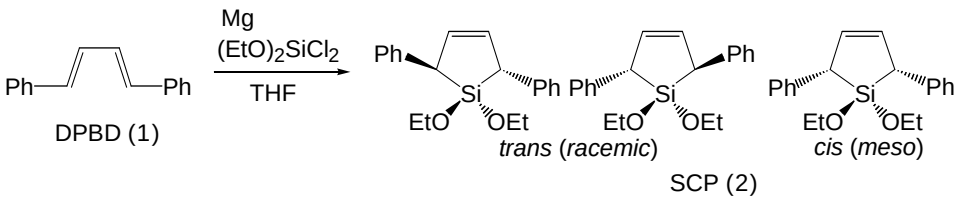
Abstract − The 1,1-diethoxy-2,5-diphenylsilacyclopent-3-ene was reacted with optically active alcohols ((-)-menthol, (-)-borneol, (-)-amyl alcohol) to obtain the corresponding 1,1-bis(optically active alkoxy)-2,5-diphenylsilacyclopent-3-enes including various ratios of diastereomers. The 1,1-diethoxy- and dialkoxy-2,5-diphenylsilacyclopent-3-enes were reacted with acetylchloride in the presence of zinc chloride to produce 1,1-dichloro-2,5-diphenylsilacyclopent-3-ene having reactive substituents including various ratios of diastreomers.

The reactions and stereochemistry of silacyclopentenes having 2,5-disubstituents and a reactive 1-substituent are of interest in organic synthesis because a large and special steric effect through the reactive silicon atom is expected. Therefore a high diastereomer selectivity was obtained in the aldol reaction of silyl enol ether by using 2,5-disubstituted silacyclopenetenes.[1] Recently, 2,5-disubstituted or 2-substituted silacyclopentenes were prepared in good yields from siloles or dialkylsilanes.[2,3] The silylation of dienes with dichlorosilanes in the presence of magnesium is the most straightforward method to prepare 2,5-disubstituted silacyclopentenes. Metallic magnesium is known to react with (1*E*,3*E*)-1,4-diphenylbuta-1,3-diene in THF to yield the halide-free organomagnesium compound,

≠ Dedicated to the memory of Professor Ekkehard Winterfeldt

1,4-diphenylbut-2-ene-1,4-diylmagnesium.[4] However, the reaction of magnesium with buta-1,3-diene or isoprene is usually accompanied by dimerization, trimerization and oligomerization.[5] Although the utilization of these organomagnesium compounds has been limited, several silacyclopentenes were prepared by reacting buta-1,3-dienes with dichlorosilanes using magnesium.[6-8] Substituted but-2-ene-1,4-diylmagnesium complexes are conveniently prepared through the reaction of activated magnesium with the corresponding 1,3-dienes. Then, dichlorodimethylsilane reacts with 1,4-diphenylbut-2-ene-1,4-diylmagnesium to give the *cis*-1,1-dimethyl-2,5-diphenylsilacyclopent-3-ene.[4, 9] Although the structure of the magnesium complex has been determined,[10] the reaction of dialkoxydichlorosilanes with the complex has not been reported. We previously reported the synthesis of the 1-substituted derivatives of 2,5-diphenylsilacyclopent-3-ene by a one-pot reaction of magnesium with (1*E*,3*E*)-1,4-diphenylbuta-1,3-diene (**1**) (DPBD) and various chlorosilanes,[11,12] and the 1,1-diethoxy-2,5-diphenylsilacyclopent-3-ene (**2**) (SCP) was obtained as a mixture of *cis* and *trans* isomers (Scheme 1). After the lithiation of 1,1-dialkoxy-2,5-diphenylsilacyclopent-3-enes with lithium diisopropyl amide (LDA), alkyl bromide is reacted and then acetic acid is reacted to give 1,1-dialkoxy-*r*-2-alkyl-2,*t*-5-diphenylsilacyclopent-3-ene, 2-alkylated *cis*-1,1-dialkoxy-2,5-diphenylsilacyclopent-3-ene, and *trans*-1,1-dialkoxy-2,5-diphenyl-silacyclopent-3-ene.[13] The stereochemistry of 2,5-diphenylsilacyclopent-3-ene and their corresponding optically active alkoxy disastereomers were investigated by using both X-ray structure analysis of *cis*-1-alkoxy-1-alkyl-2,5-diphenylsilacyclopent-3-ene and NOE in NMR experiments.[14] Optically active silacyclopent-3-enes are obtainable by isolating from their derivatives of diastereomers and the special steric effect on the reactions of optically active derivatives are very useful.



Scheme 1

In this paper, the preparation and stereochemistry of 1,1-dialkoxy-2,5-diphenylsilacyclopent-3-ene (**3**) by the reactions of 1,1-diethoxy-2,5-diphenylsilacyclopent-3-ene (**2**) with optically active alcohols were

described (Scheme 2). Then the reactions of diethoxysilacyclopentene (**2**) and dialkoxysilacyclopentenes (**3**) with acetyl chloride were investigated to produce 1,1-dichloro-2,5-diphenylsilacyclopent-3-ene (**4**) (Scheme 3).

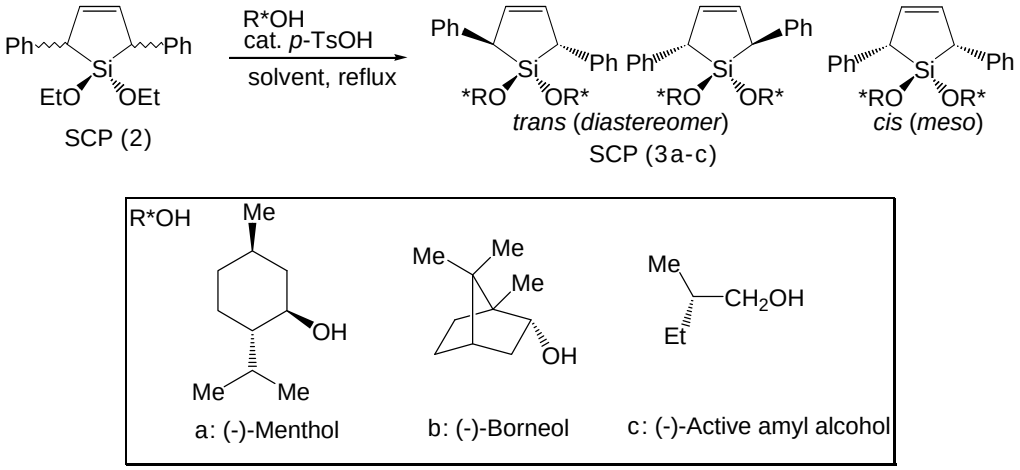
RESULTS AND DISCUSSION

Synthesis of diastereomeric 1,1-diethoxy and 1,1-bis(optically active alkoxy)substituted 2,5-diphenylsilacyclopent-3-enes (**2** and **3**) were performed. The yield and isomer ratio of diethoxysilacyclopentene (**2**) is shown in Table 1 (Scheme 1). The reaction of diethoxysilacyclopentene (**2**) with optically active alcohols ((–)-menthol, (–)-borneol , and (–)-amyl alcohol) in various solvents in the presence of *p*-toluenesulfonic acid (*p*-TsOH) gave the corresponding disastereomers (**3a-c**). The reactions conditions, yields, and isomer ratios are shown in Table 2 (Scheme 2). The yields and isomer ratios were changed by the reaction conditions. The yields increased by changing solvent (hexane,

Table 1. Preparations of silacyclopentene **2**[a]

Temp. (ºC)	Time (h)	Product	Yield (%) [b]	Isomer ratio [c] *trans* : *cis*
67 (reflux)	41	**2**	83	58 : 42

[a]Molar ratio: DPBD **1** : $(EtO)_2SiCl_2$: Mg = 1 : 1 : 1.1.
[b]Isolated yields by distillation. The product was fully characterized by ^{1}H-NMR, ^{13}C-NMR, ^{29}Si-NMR, IR and mass spectra.
[c]Isomer ratio was determined by ^{1}H-NMR analysis of products.



Scheme 2

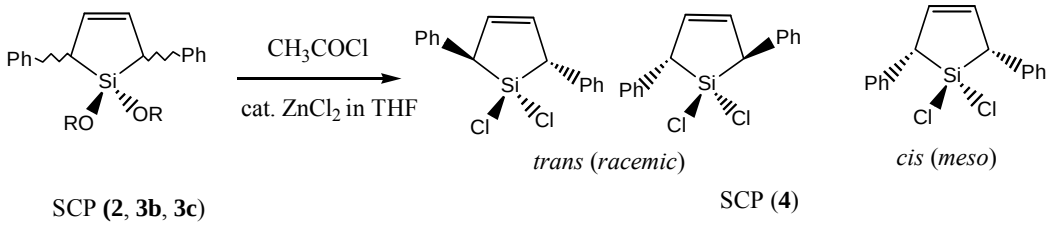
benzene and toluene) to rise reaction temperature. In the reaction with (–)-borneol, the isomer ratios of *trans* form increased at higher reaction temperature in mesitylene. The change of isomer ratio is caused by the rearrangement or different reactivity of diastereomers.

Table 2. Yield and isomer ratio of silacyclopentene **3a-c**[a]

Optically active alcohol R*OH	Solvent	Temp. (ºC)	Time (h)	Product	Yield[b] (%)	Isomer ratio[c] *trans* : *cis*
(–)-menthol	hexane	69 (reflux)	7	**3a**	29	58 : 42
(–)-menthol	benzene	80 (reflux)	20	**3a**	41	58 : 42
(–)-menthol	toluene	110 (reflux)	20	**3a**	66	58 : 42
(–)-borneol	toluene	110 (reflux)	61 (20)	**3b**	71 (68)	58 : 42
(–)-borneol	mesitylene	164 (reflux)	20	**3b**	53	64 : 36
(−)-borneol	mesitylene	164(reflux)	40	**3b**	40	76 : 24
(–)-active amyl alcohol	toluene	110 (reflux)	40	**3c**	66	63 : 37
(–)-active amyl alcohol	mesitylene	120 (reflux)	40	**3c**	50	63 : 37

[a]Molar ratio: SCP **2** : R*OH : *p*-TsOH = 1 : 4 : 0.03.
[b]Isolated yields by distillation. The product was fully characterized by ^{1}H-NMR, ^{13}C-NMR, ^{29}Si-NMR, IR and mass spectra.
[c]Isomer ratio was determined by ^{1}H-NMR analysis of products.

Chlorination of dialkoxy-2,5-diphenylsilacyclopent-3-enes were performed by the reaction of diethoxy and dialkoxysilacyclopentenes (**2** and **3**) with acetylchloride. The reaction of diethoxysilacyclopentene (**2**) with acetyl chloride in the presence of zinc chloride gave the 1,1-dichloro-2,5-diphenylsilacyclopent-3-ene (**4**) in high yield. The dialkoxysilacyclopentene (**3b** and **3c**) gave dichlorosilacyclopentene (**4**) by a similar method and the yields are shown in Table 3 (Scheme 3). The reaction of menthoxy silacyclopentene **3a** gave a mixtue containing many kind of products and dichlorosilacyclopentene **4** was



SCP (**2**, **3b**, **3c**) *trans* (*racemic*) SCP (**4**) *cis* (*meso*)

Scheme 3

not isolated. In ^{1}H-NMR spectra of silacyclopentene (**2** and **4**), both methine peaks (CHφ and CH=) of dichlorosilacyclopentene (**4**) were shifted to lower field than peaks of diethoxysilacyclopentene (**2**) because of lower electron back donation of chlorine atoms to silicon atom. The isomer ratios of **4** were similar to the ratios of corresponding dialkoxysilacyclopentenes. Therefore rearrangement is not founded in these reactions. The chlorination of each separated and isolated diastereomer is possible by this reaction without rearrangement.

Table 3. Chlorination of silacyclopentene **2**,**3b**, and **3c**[a]

SCP	Temp. (ºC)	Time (h)	Product	Yield[b] (%)	Isomer ratio[c] *trans* : *cis*
2	rt	40	**4**	79	52 : 48
2	rt	160	**4**	86	60 : 40
3b	rt	63	**4**	60	61 : 39
3b	rt	160	**4**	94	62 : 38
3c	rt	160	**4**	92	59 : 41

[a]Molar ratio: SCP : CH_3COCl : $ZnCl_2$ = 1 : 10.5 : 0.004.
[b]Isolated yields by distillation. The product was fully characterized by ^{1}H-NMR, ^{13}C-NMR, ^{29}Si-NMR, IR and mass spectra.
[c]Isomer ratio was determined by ^{1}H-NMR analysis of products.

CONCLUSION

The *cis* and *trans* 1,1-diethoxy-2,5-diphenylsilacyclopent-3-enes react with optically active alcohols to give diastereomeric *cis* and *trans*-1,1-disubstituted deriveatives of 2,5-diphenylsilacyclopent-3-ene. The mixture of *trans* and *cis* isomers of 1,1-diethoxy-2,5-diphenylsilacyclopent-3-ene can be directly reacted with optically active alcohol in mesitylene at high reflux temperature to give a high rato of diastereomeric *trans*-1,1-disubstituted deriveatives of 2,5-diphenylsilacyclopent-3-ene. Both 1,1-diethoxy and 1,1-bis(optically active alkoxy) of 2,5-diphenylsilacyclopent-3-ene can be reacted with acetyl chloride in the presence of zinc chloride to give the 1,1-dichloro-2,5-dipheny-lsilacyclopent-3-ene having reactive substituents.

EXPERIMENTAL

General

All reactions were carried out under dry nitrogen atmosphere, unless otherwise noted. ^{1}H-NMR(500MHz

or 300MHz), ^{13}C-NMR(125MHz or 99MHz) and ^{29}Si-NMR(99MHz or 60MHz) spectra were recorded with a JOEL JNM-EPC-500 or JNM-EPC-300 spectrometer in $CDCl_3$. The stereochemistry of the isomers was assigned on the basis of NMR spectra. Mass spectra was recorded with a JOEL JMS-SX102A spectrometer. Column chromatography was performed using Wakogel C-200 (75-150μm) (Wako Pure Chemical Industries, Ltd.), and components were located by observation under UV light. Tetrahydrofuran, benzene, toluene and acetone were used commercially available dehydrated solvents. Zinc chloride was used commercially available solvent, 0.5N $ZnCl_2$ in THF (Sigma-Aldrich Corp.).

Preparation of 1,1-diethoxy-2,5-diphenylsilacyclopent-3-ene (2)

Preparation of 1,1-diethoxy-2,5-diphenylsilacyclopent-3-ene (SCP) was described in a previous procedure[11]: Dichlorodiethoxysilanes (200 mmol) in THF (60 mL) was dropped to a mixture of (1*E*,3*E*)-1,4-diphenylbuta-1,3-diene (**1**) (200 mmol) and magnesium pretreated at 200 ℃ under nitrogen (for Grignard reactions 220 mmol) in THF (220 mL) at rt. The mixture was stirred at reflux temperature (67 ºC) for 41 h. After evaporation of THF from the reaction mixture and adding benzene, the residue was removed by filtration. The filtrate was evaporated in order to remove solvent, and the precipitate was distilled under reduced pressure to give 1,1-diethoxy-2,5-diphenylsilacyclopent-3-ene (**2**).

1,1-Diethoxy-2,5-diphenylsilacyclopent-3-ene (**2**):

Compound **2** was obtained in 83% isolated yield; Appearance: green-tinged yellow liquid; Bp 138-139 ℃ /0.4 mmHg; ^{1}H-NMR (300MHz, $CDCl_3$): *trans*, δ_H = 7.27-7.08 (10H, m, aryl CH), 6.23 (2H[58%], s, 1-ethylene =CH), 3.36 (2H[58%], q, *J* = 6.9 Hz, methylene O$\underline{CH_2}CH_3$), 3.24 (2H[58%], q, 6.9, methylene O$\underline{CH_2}CH_3$), 3.26 (2H[58%], s, methine CHφ), 0.82 (6H[58%], t, *J* = 7.0 Hz, methyl $OCH_2\underline{CH_3}$) ppm; *cis*, δ_H = 7.27-7.08 (10H, m, aryl CH), 6.17 (2H[42%], s, 1-ethylene =CH), 3.94 (2H[42%], q, *J* = 6.9 Hz, methylene O$\underline{CH_2}CH_3$), 2.95 (2H[42%], q, *J* = 6.9 Hz, methylene O$\underline{CH_2}CH_3$), 3.13 (2H[42%], s, methine CHφ), 1.31 (3H[42%], t, *J* = 7.0 Hz, methyl $OCH_2\underline{CH_3}$), 0.48 (3H[42%], t, *J* = 7.0 Hz, methyl $OCH_2\underline{CH_3}$) ppm; ^{13}C-NMR (75 MHz, $CDCl_3$): δ_C = 141.5, 141.2 [*cis*, *trans*] (C, 1-benzene), 135.0, 134.3 [*trans*, *cis*] (CH, 1-ethylene =CH), 128.3, 128.2 [*trans*, *cis*] (CH, 1-benzene), 127.2, 127.0 [*cis*, *trans*] (CH, 1-benzene), 124.7, 124.6 [*trans*, *cis*] (CH, 1-benzene), 59.4, 59.1, 59.0 [*cis*, *trans*, *cis*] (CH_2, methylene), 35.4, 35.0 [*cis*, *trans*] (CH, methine), 18.4, 17.7, 17.3 [*cis*, *trans*, *cis*] (CH_3, methyl) ppm; ^{29}Si-NMR (99MHz, $CDCl_3$): δ_{Si} = –9.6 [*cis*], –11.1 [*trans*] ppm; MS (Ion mode: EI^+) *m/z*: 324 $(M)^+$. Anal. Calcd for $C_{20}H_{24}O_2Si$: C 74.03, H

7.45. Found: C 74.38, H 7.43.

Reaction of 1,1-diethoxy-2,5-diphenylsilacyclopent-3-ene (2) with optically active alcohol

Preparation of 1,1-bis(optically active alkoxy)-2,5-diphenylsilacyclopent-3-enes (**3**) were investigated by previous procedure[10, 13] with a little arrangement: In most examples, a solution of SCP **2** (9.26 mmol), (–)-active amyl alcohol (37.0 mmol) and *p*-TsOH (0.03 mmol) in toluene (5 mL) was refluxed for 20 h. The resulting solution was distilled under reduced pressure, and the residue was purified by silica gel column chromatography (eluent: hexane/$CHCl_3$=1/1) to afford the corresponding SCP **3c**. The reaction of **2** with (–)-menthol in hexane, benzene or toluene gave **3a**, **2** with (–)-borneol in toluene or mesitylene gave **3b**, and **2** with (–)-active amyl alcohol in mesitylene gave **3c** by a similar method.

1,1-Bis((1'*R*,2'*S*,5'*R*)-2'-isopropyl-5'-methylcyclohexyloxy)-2,5-diphenylsilacyclopent-3-ene (**3a**):

Compound **3a** was obtained in 66% isolated yield; Appearance: green yellow liquid; Bp 208.2-211.9 ℃ /0.18 mmHg; ^{1}H-NMR (400MHz, $CDCl_3$): *trans*, δ_H = 7.25-7.08 (10H, m, aryl CH), 6.24, 6.23 [*transA**, *transB**] (2H[58%], s, 1-ethylene =CH), 3.23, 3.19 [*transA**, *transB**] (2H[58%], s, methine CHφ), 3.42-3.37 (1H[58%], m, methine OCH), 3.37-3.30 (1H[58%], m, methine OCH), 2.10-2.02 (2H[58%], m, methine $\underline{CH}(CH_3)_2$), 1.77-0.22 (34H, m, alkyl-bridge CH_2,CH, methyl CH_3) ppm; *cis*, δ_H = 7.25-7.08 (10H, m, aryl CH), 6.15 (2H[42%], s, 1-ethylene =CH), 3.10 (2H[42%], s, methine CHφ), 3.83-3.79 (1H[42%], m, methine OCH), 2.95-2.84 (1H[42%], m, methine OCH), 2.39-2.30 (1H[42%], m, methine $\underline{CH}(CH_3)_2$), 1.80-1.75 (1H[42%], m, methine $\underline{CH}(CH_3)_2$), 1.77-0.22 (34H, m, alkyl-bridge CH_2,CH, methyl CH_3) ppm; MS (Ion mode: EI^+) *m/z*: 544 $(M)^+$. Anal. Calcd for $C_{36}H_{52}O_2Si$: C 79.35, H 9.62. Found: C 78.94, H 9.43.

1,1-Bis((1'*S*,2'*R*,4'*S*)-1',7',7'-trimethylbicyclo[2.2.1]heptan-2'-oxy)-2,5-diphenylsilacyclopent-3-ene (**3b**):

Compound **3b** was obtained in 68% isolated yield; Appearance: green-tinged yellow liquid; Bp 205.0-209.0 ℃/0.20 mmHg; ^{1}H-NMR (500 MHz, $CDCl_3$): *trans*, δ_H = 7.25-7.05 (10H, m, aryl CH), 6.23 (2H[58%], s, 1-ethylene =CH), 3.94-3.90 (2H[58%], m, methine OCH), 3.22, 3.20 [*transA**, *transB**] (2H[58%], s, methine CHφ), 1.94-1.82 (2H[58%], m, alkyl-bridge CH_2,CH), 1.80-0.05 (12H, m, *cis, trans*, alkyl-bridge CH_2,CH), 0.58 (3H[58%], s, methyl CH_3), 0.57 (3H[58%], s, methyl CH_3), 0.70 (6H[58%], s, methyl CH_3), 0.76 (3H[58%], s, methyl CH_3), 0.75 (3H[58%], s, methyl CH_3) ppm; *cis*, δ_H = 7.25-7.05 (10H, m, aryl CH), 6.16 (2H[42%], s, 1-ethylene =CH), 4.35-4.32 (1H[42%], m, methine OCH), 3.53-3.50

(1H[42%], m, methine OCH), 3.11-3.08 (2H[42%], m, methine CHφ), 2.42-2.36 (1H[42%], m, alkyl-bridge CH_2,CH), 2.15-2.09 (1H[42%], m, alkyl-bridge CH_2,CH), 1.80-0.05 (12H, m, *cis, trans*, alkyl-bridge CH_2,CH), 0.96 (3H[42%], s, methyl CH_3), 0.93 (3H[42%], s, methyl CH_3), 0.59 (3H[42%], s, methyl CH_3), 0.46 (3H[42%], s, methyl CH_3), 0.91 (3H[42%], s, methyl CH_3), 0.19 (3H[42%], s, methyl CH_3) ppm; ^{13}C-NMR (75MHz, $CDCl_3$): δ_C = 142.02, 141.84, 141.82, 141.76 [*cis*, *cis*, *trans*, *trans*] (C, 1-benzene), 135.10, 134.48, 134.36 [*trans*, *cis*, *cis*] (CH, 1-ethylene =CH), 128.22, 128.19, 128.18, 128.12 [*trans*, *cis*, *trans*, *cis*] (CH, 1-benzene), 127.31, 127.18 [*cis*, *trans*] (CH, 1-benzene), 124.52, 124.50, 124.48, 124.45 [*trans*, *trans*, *cis*, *cis*] (CH, 1-benzene), 78.24, 78.15, 78.12 [*cis*, *trans*, *cis*] (C, alkyl-bridge $C(CH_3)_2$), 50.09, 49.67, 49.66, 49.21 [*cis*, *trans*, *trans*, *cis*] (CH, alkyl-bridge CCH_3, OCH or CH), 47.53, 47.20, 46.94 [*cis*, *trans*, *cis*] (CH, alkyl-bridge CCH_3, OCH or CH), 45.32, 45.07, 45.05, 44.76 [*cis*, *trans*, *trans*, *cis*] (CH, alkyl-bridge CCH_3, OCH or CH), 39.57, 38.83, 38.78, 37.85 [*cis*, *trans*, *trans*, *cis*] (CH, alkyl-bridge CH_2), 35.84, 35.79, 35.58, 35.50 [*cis*, *trans*, *trans*, *cis*] (CH, methine), 28.33, 28.10, 28.06, 27.68 [*cis*, *trans*, *trans*, *cis*] (CH, alkyl-bridge CH_2), 26.30, 25.90, 25.81, 25.40 [*cis*, *trans*, *trans*, *cis*] (CH, alkyl-bridge CH_2), 20.21, 20.08, 19.95 [*cis*, *trans*, *cis*] (CH_3, methyl), 18.88, 18.68, 18.47 [*cis*, *trans*, *cis*] (CH_3, methyl), 13.86, 13.38, 13.21, 12.58 [*cis*, *trans*, *trans*, *cis*] (CH_3, methyl) ppm; ^{29}Si-NMR (99MHz, $CDCl_3$): δ_{Si} = –11.7 [*cis*], –15.5 [*transA**], –16.3 [*transB**] ppm; MS (Ion mode: EI^+) *m/z*: 540 $(M)^+$. Anal. Calcd for $C_{36}H_{48}O_2Si$: C 79.95, H 8.95. Found: C 79.67, H 8.85.

1,1-Bis((2'*S*)-2'-methylbutoxy)-2,5-diphenylsilacyclopent-3-ene (**3c**):

Compound **3c** was obtained in 66% isolated yield; Appearance: green-tinged yellow liquid; Bp 157.0-165.0 ℃/0.080 mmHg; ^{1}H-NMR (300MHz, $CDCl_3$): *trans*, δ_H = 7.36-7.08 (10H, m, aryl CH), 6.24 (2H[63%], s, 1-ethylene =CH), 3.32-2.96 (2H[63%], m, methine OCH_2), 3.25 (2H[63%], s, methine CHφ), 1.77-0.47 (3H, m, aliphatic CH_2,CH), 0.65 (3H[63%], d, *J* = 6.3 Hz, methyl CH_3), 0.63 (3H[63%], d, *J* = 6.3 Hz, methyl CH_3), 0.73 (6H[63%], t, *J* = 6.9 Hz, methyl CH_3) ppm; *cis*, δ_H = 7.36-7.08 (10H, m, aryl CH), 6.17 (2H[37%], s, 1-ethylene =CH), 3.80-3.62 (1H[37%], m, methine OCH_2), 2.80-2.65 (1H[37%], m, methine OCH_2), 3.13 (2H[37%], s, methine CHφ), 1.77-0.47 (3H, m, aliphatic CH_2,CH), 0.97 (3H[37%], d, *J* = 6.3 Hz, methyl CH_3), 0.32 (3H[37%], d, *J* = 6.3 Hz, methyl CH_3), 0.84 (3H[37%], t, *J* = 6.9 Hz, methyl CH_3), 0.52 (3H[37%], t, *J* = 6.9 Hz, methyl CH_3) ppm; ^{13}C-NMR (125MHz, $CDCl_3$): δ_C = 141.69, 141.43,

141.41 [*cis*, *trans, trans*] (C, 1-benzene), 135.05, 134.38 [*trans*, *cis*] (CH, 1-ethylene =CH), 128.32, 128.16 [*trans*, *cis*] (CH, 1-benzene), 127.30, 127.08 [*cis*, *trans*] (CH, 1-benzene), 124.65, 124.55 [*trans*, *cis*] (CH, 1-benzene), 68.68, 68.21, 68.19, 67.48 [*cis*, *trans*, *trans*, *cis*] (CH, methane OCH_2), 37.31, 36.81, 36.47 [*cis*, *trans*, *cis*] (CH, aliphatic CH), 35.25, 34.85, 34.80 [*cis*, *trans*, *trans*] (CH, methine), 25.82, 25.48, 25.04 [*cis*, *trans*, *cis*] (CH, aliphatic CH_2), 16.28, 15.92, 15.85, 15.47 [*cis*, *trans*, *trans*, *cis*] (CH_3, methyl), 11.42, 11.26, 11.25, 11.09 [*cis*, *trans*, *trans*, *cis*] (CH_3, methyl) ppm; ^{29}Si-NMR (99MHz, $CDCl_3$): δ_{Si} = –10.5 [*cis*], –12.9 [*transA**], –13.0 [*transB**] ppm; MS (Ion mode: FAB^+) *m/z*: 409 $(M+H)^+$; HRMS (Ion mode: FAB^+) *m/z*: Calcd for $C_{26}H_{36}O_2Si$: 408.2485. Found: 408.2478.

Chlorination of 1,1-diethoxy and dialkoxy-2,5-diphenylsilacyclopent-3-ene (2, 3b , and 3c)

SCP **2** (9.26 mmol) and acetyl chloride (97.2 mmol) were stirred at rt and dropped 0.5 M zinc chloride in THF (0.04 mmol) in ice bath. The reaction mixture was stirred at rt for 160 h. After carrying out reduced pressure distilling off of the acetylchloride used superfluously from reaction mixture, hexane (5 mL) were added, and the residual liquid stirred for 1 h. The reaction mixture was purified by distillation under reduced pressure to give 1,1-dichloro-2,5-diphenylsilacyclopent-3-ene (**4**).

1,1-Dichloro-2,5-diphenylsilacyclopent-3-ene (**4**):

Compound **4** was obtained in 86% isolated yield; Appearance: yellow liquid; Bp 140-142 ºC/0.08 mmHg; ^{1}H-NMR (300 MHz, $CDCl_3$): *trans,* δ_H = 7.25-6.98 (10H, m, aryl CH), 6.36 (2H[52%], s, 1-ethylene =CH), 3.70 (2H[52%], s, methine CHφ) ppm; *cis,* δ_H = 7.25-6.98 (10H, m, aryl CH) 6.29 (2H[48%], s, 1-ethylene =CH), 3.65 (2H[48%], s, methine CHφ) ppm; ^{13}C-NMR (75MHz, $CDCl_3$): δ_C = 138.1, 137.6 [*cis*, *trans*] (C, 1-benzene), 134.1, 133.4 [*trans*, *cis*] (CH, 1-ethylene =CH), 128.6, 128.6 [*trans*, *cis*] (CH, 1-benzene), 127.3, 127.2 [*trans*, *cis*] (CH, 1-benzene), 127.1, 127.1 [*cis*, *trans*] (CH, 1-benzene), 126.0, 126.0 [*trans*, *cis*] (CH, 1-benzene), 41.7, 41.0 [*cis*, *trans*] (CH, methine) ppm; ^{29}Si-NMR (60MHz, $CDCl_3$): δ_{Si} = 24.6 [*trans*], 21.0 [*cis*] ppm; IR ν_{max} (neat): 594, 575, 526**** (Si-Cl) cm^{-1}; MS (Ion mode: EI^+) *m/z*: 304 $(M)^+$, 306 $(M+2)^+$, 308 $(M+4)^+$; HRMS (Ion mode: EI^+) *m/z*: Calcd for $C_{16}H_{14}{}^{35}Cl_2Si$: 304.0242. Found: 304.0237. Anal. Calcd for $C_{16}H_{14}Cl_2Si$: C 62.95, H 4.62. Found: C 62.91, H 4.62. SCP **3b** and and **3c** were reacted by similar method to give dichloro compound **4**.

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