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SYNTHESIS OF NOVEL SILACYCLOBUTENE DERIVATIVES UTILIZING ZIRCONOCENE- AND TITANOCENE-ETHYLENE COMPLEXES

Chung Keun Jin,[a] Tinh Van Dang,[a] Yoshifumi Ikee,[a] Toshiaki Yamada,[a] Shigeki Sano,[a] Motoo Shiro,[b] and Yoshimitsu Nagao*,[a]

[a]Graduate School of Pharmaceutical Sciences, The University of Tokushima,
Sho-machi, Tokushima 770-8505, Japan.
[b]Rigaku Corporation, 3-9-12 Matsubara-cho, Akishima, Tokyo 196-8666, Japan.
E-mail: ynagao@ph.tokushima-u.ac.jp

Abstract – New types of silacyclobutene derivatives were synthesized by zirconocene- and titanocene-ethylene complexes-promoted reactions of some *rac*-dialkynyldiarylsilanes.

The organosilicon compounds such as aryl-, vinyl-, and alkynyldisilanes, silacyclobutanes, and silacyclobutenes have been interested since 1979, when Brook and co-workers reported synthesis of the stable silenes.[1] In general, silacyclobutenes can be synthesized by [2+2] cycloaddition of alkynes with silenes.[2] Several years ago, Takahashi and co-workers reported an interesting synthetic method for the silacyclobutene derivatives utilizing the reaction of bis(alkynyl)silanes with a zirconocene-ethylene complex.[3] However, the only bis(alkynyl)silanes bearing the same alkynyl groups were exclusively employed for the zirconocene-mediated reactions. Recently, we have developed an efficient synthetic procedure for the dialkynyldiarylsilanes bearing different kinds of dialkynyl groups,[4] which seemed to be useful for the synthesis of new types of silacyclobutenes. In this paper, we describe synthesis of new types of silacyclobutene derivatives (**2a**-**c** and **3a**-**c**) utilizing zirconocene-mediated intramolecular C-C bond formation between two different alkynyl groups of *rac*-dialkynyldiarylsilanes (**1a**-**c**) followed by acidification of the resulting four-membered ziroconacyclobutene intermediates (**A** and **B**), as shown in Scheme 1. Namely, a THF solution of zirconocene-ethylene complex $Cp_2Zr(CH_2{=}CH_2)$, prepared *in situ* by reaction of Cp_2ZrCl_2 with EtMgBr in THF at -60 °C, was added to a solution of phenyl(2,4,6-triisopropylphenyl)(*t*-butylethynyl)((2,4,5-trimethylphenyl)ethynyl)silane (**1a**) in THF at -60 °C.[3] The mixture was allowed to warm up gradually to room temperature over 1 h with stirring and

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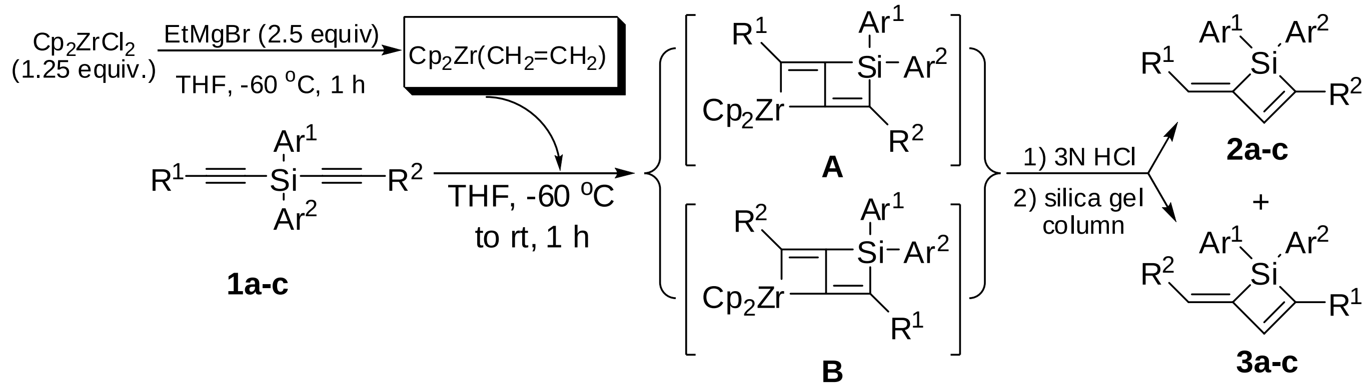
† Dedicated to Dr. Steven M. Weinreb (Professor of The Pennsylvania State University) in celebration of his 65th birthday

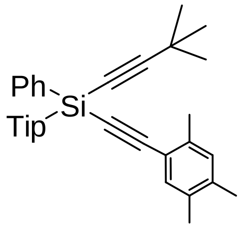
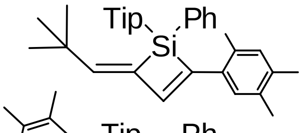
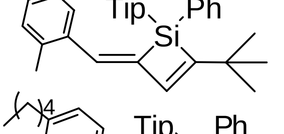
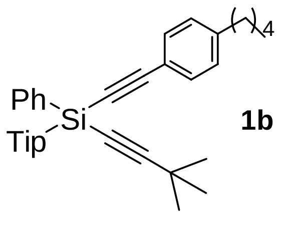
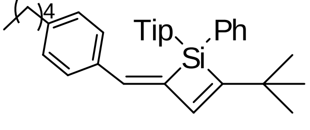
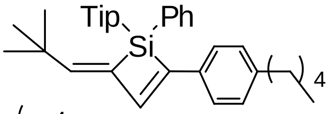
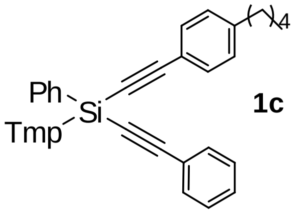
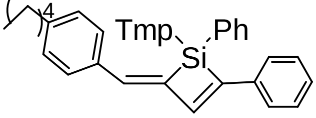
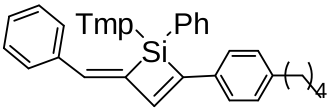
then stirred for additional 1 h to form zirconacyclobutene-silacyclobutene intermediates (**A** and **B**).[3] The crude intermediates (**A** and **B**) were treated with 3N HCl to afford two kinds of silacyclobutenes (**2a**) (53% yield) and (**3a**) (16% yield) after chromatographic separation of the regioisomeric mixture on a silica gel column with *n*-hexane-CHCl$_3$ (10:1) (Table 1, Entry 1).



Scheme 1

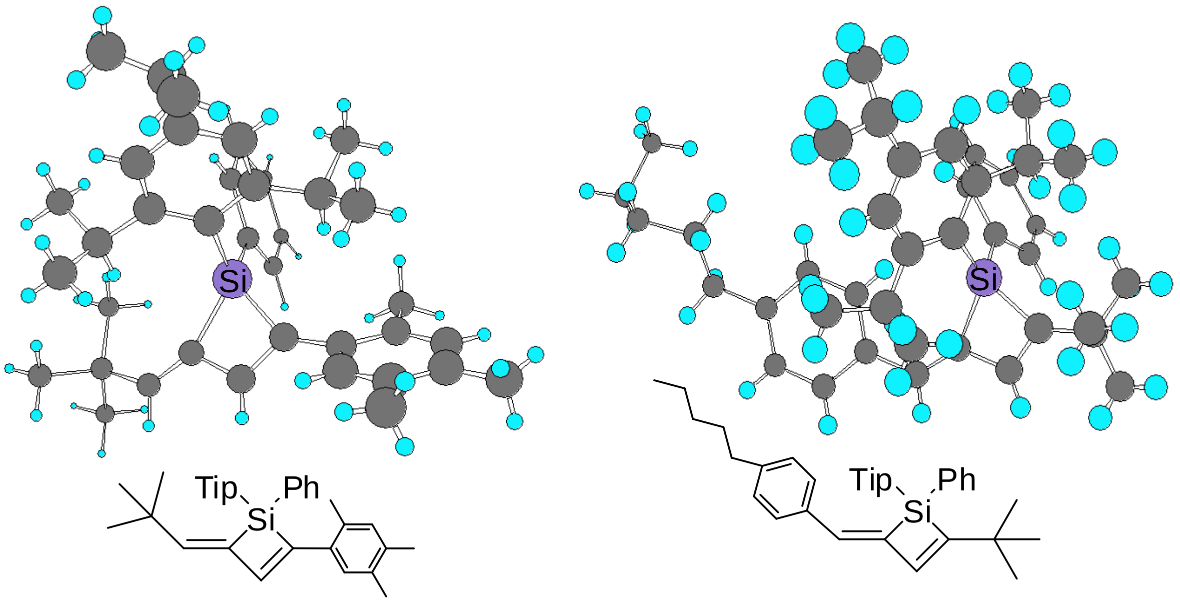
The same treatment of **1b** as described above, afforded **2b** in 53% yield and **3b** in 14% yield, respectively (Table 1, Entry 2). In the case of **1c,** an inseparable mixture of silacyclobutenes (**2c** and **3c**) was obtained in 78% total yield with a 1:1 (**2c** : **3c**) ratio (Table 1, Entry 3).

Table 1. Synthesis of New Silacyclobutenes Utilizing the Takahashi Zirconocene-Ethylene Complex.

Entry	Dialkynylsilanes		Product^a		Yield (%)^b
1		**1a**		**2a**	53
				**3a**	16
2		**1b**		**2b**	53
				**3b**	14
3^c		**1c**		**2c**	78
				**3c**	

^{a}Tip = 2,4,6-triisopropylphenyl, Tmp = 2,4,6-trimethylphenyl. ^{b} Isolated yields.
^{c} A 1:1 (**2c** : **3c**) ratio was determined by ^{1}H NMR (400 MHz, CDCl$_3$) analysis.

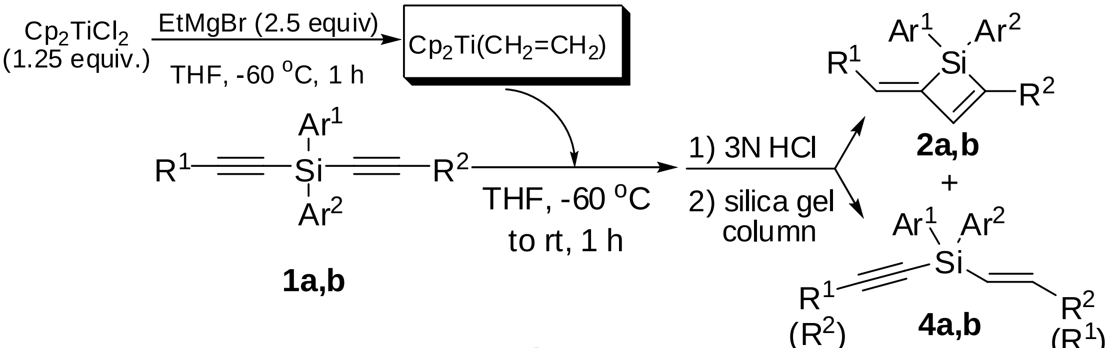
The structures of silacyclobutene derivatives (**2a** and **2b**) were precisely determined by X-Ray crystallographic analyses, as shown in Figure 1.[5] Other products were assigned to be the structures (**2c** and **3a-c)** based on the characteristic data of spectroscopic and elemental analyses in comparison with those of the compounds (**2a** and **2b**).



2a **2b**

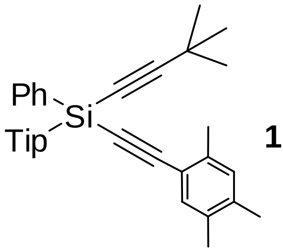
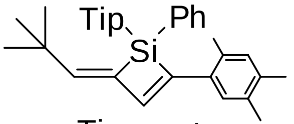
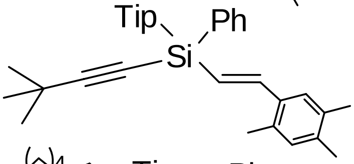
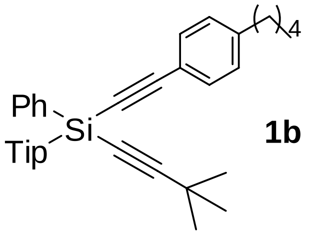
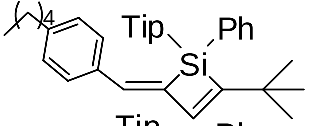
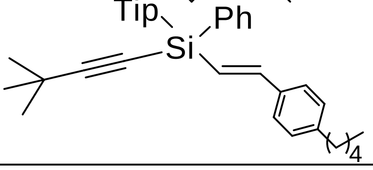
Figure 1. Computer-generated drawing derived from the X-Ray coordinates of compounds (**2a** and **2b**)

Tentative reactions of dialkynyldiarylsilanes (**1a,b**) with titanocene-ethylene complex $Cp_2Ti(CH_2{=}CH_2)$, prepared *in suit* by reaction of Cp_2TiCl_2 with EtMgBr in THF at -60 °C, were carried out in comparison with the cases of the zirconocene-ethylene complex. The reactions gave the corresponding silacyclobutenes (**2a,b**) in low yields together with hydrogenated compounds of **1a,b,** as shown in Scheme 2 and Table 2. The structures of the hydrogenated compounds (**4a,b**) bearing the *E*-type of olefinic moiety (**4a**: J = 14.4 Hz, **4b**: J = 15.1 Hz) were determined by their ^{1}H NMR analyses, HSQC and HMBC experiments.[6] In the HMBC NMR spectrum of **4a**, the proton at δ 6.13 (Si-C$\underline{\text{H}}$=CH-) ppm showed long-range correlations with carbon signals at δ 80.14 (≡$\underline{\text{C}}$-Si), 135.68 (=CH-$\underline{\text{Ph}}$), and 144.78 (Si-CH=$\underline{\text{C}}$H-) ppm. In the case of **4b**, the proton at δ 6.12 (Si-C$\underline{\text{H}}$=CH-) ppm showed long-range correlations with carbon signals at δ 80.37 (≡$\underline{\text{C}}$-Si), 136.14 (=CH-$\underline{\text{Ph}}$), and 146.04 (Si-CH=$\underline{\text{C}}$H-) ppm. The different reaction mechanisms between zirconocene- and titanocene-complex-promoted reactions of **1a,b** are unclear.



Scheme 2

Table 2. Synthesis of Silacyclobutenes Utilizing Tirconocene - Ethylene Complex.

Entry	Dialkynylsilanes		Product[a]		Yield (%)[b]
1		**1a**		**2a**	5
				**4a**[c]	44
2		**1b**		**2b**	4
				**4b**[c]	52

[a] Tip = 2,4,6-triisopropylphenyl, Tmp = 2,4,6-trimethylphenyl. [b] Isolated yields.
[c] Determined by HSQC and HMBC experiments.

In conclusion, we have demonstrated that the reactions of different kinds of dialkynyldiarylsilanes with a zirconocene complex gave new types of silacyclobutene derivatives as a mixture of the regioisomers. The similar reactions of the dialkynyldiarylsilanes with a titanocene complex afforded a small amount of silacyclobutenes and hydrogenated products of the starting compounds.

ACKNOWLEDGEMENTS

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4. Unpublished results.
5. The crystallographic data of compounds (**2a** and **2b**).
   2a: $C_{38}H_{50}Si$. MW = 534.90, colorless block, monoclinic, space group $P2_1/n$(#14), a = 18.8910(7) Å, b = 8.6064(3)Å, c = 21.1085(6)Å, V = 3309.40(19)Å^3, β = 105.3542(11)°, Z = 4, Dcalc = 1.073 g/cm^3, R = 0.0549, Rw = 0.1583; **2b**: $C_{40}H_{54}Si$. MW = 562.95, colorless block, triclinic, space group P-1(#2), a = 10.6631(3)Å, b = 12.5388(4)Å, c = 26.4981(7)Å, β = 86.9610(8)°, Z = 4, Dcalc = 1.062g/cm^3, R = 0.0825, Rw = 0.2421.
6. **4a**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65-7.63 (m, 2H), 7.44-7.40 (d, 1H, *J* = 14.4 Hz), 7.33-7.28 (m, 3H), 7.06 (s, 2H), 6.81 (s, 1H), 6.66 (s, 1H), 6.13-6.10 (d, 1H, *J* = 14.4 Hz), 3.60-3.50 (sept, 2H, *J* = 6.6 Hz), 2.96-2.86 (sept, 1H, *J* = 7.1 Hz), 2.24 (s, 3H), 2.09 (s, 3H), 1.64 (s, 3H), 1.29-1.27 (d, 6H, *J* = 7.1 Hz), 1.14-1.13 (d, 6H, *J* = 6.6 Hz), 1.07-1.05 (d, 6H, *J* = 6.6 Hz), 0.88 (s, 9H). ^{13}C NMR (100MHz, $CDCl_3$) δ 156.01, 150.58, 144.78, 138.53, 135.95, 135.68, 134.93, 132.89, 132.76, 131.03, 130.69, 129.88, 128.96, 128.94, 127.64, 121.73, 116.16, 80.14, 34.52, 33.76, 30.56, 28.12, 25.36, 24.93, 24.21, 24.08, 19.38, 18.94. **4b**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64-7.61 (m, 2H), 7.33-7.30 (m, 4H), 7.22-7.20 (d, 2H, *J* = 8.1 Hz), 7.02 (s, 2H), 6.95-6.93 (d, 2H, *J* = 8.1 Hz), 6.12-6.08 (d, 1H, *J* = 15.1 Hz), 3.69-3.62 (sept, 2H, *J* = 6.6 Hz), 2.93-2.84 (sept, 1H, *J* = 7.1 Hz), 2.52-2.48 (t, 2H, *J* = 7.6 Hz), 1.57-1.48 (m, 2H), 1.33-1.22 (m, 10H), 1.17-1.13 (d, 6H, *J* = 6.6 Hz), 1.03-1.01 (d, 6H, *J* = 6.6 Hz), 0.93 (s, 9H), 0.88-0.83 (t, 3H, *J* = 7.1 Hz). ^{13}C NMR (100MHz, $CDCl_3$) δ 156.34, 150.50, 146.04, 142.35, 138.72, 136.14, 134.73, 129.36, 129.16, 128.96, 127.69, 127.59, 127.15, 121.74, 117.06, 80.37, 35.90, 34.34, 33.42, 31.74, 31.36, 30.55, 28.29, 25.32, 25.02, 24.04, 22.76, 14.23.