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

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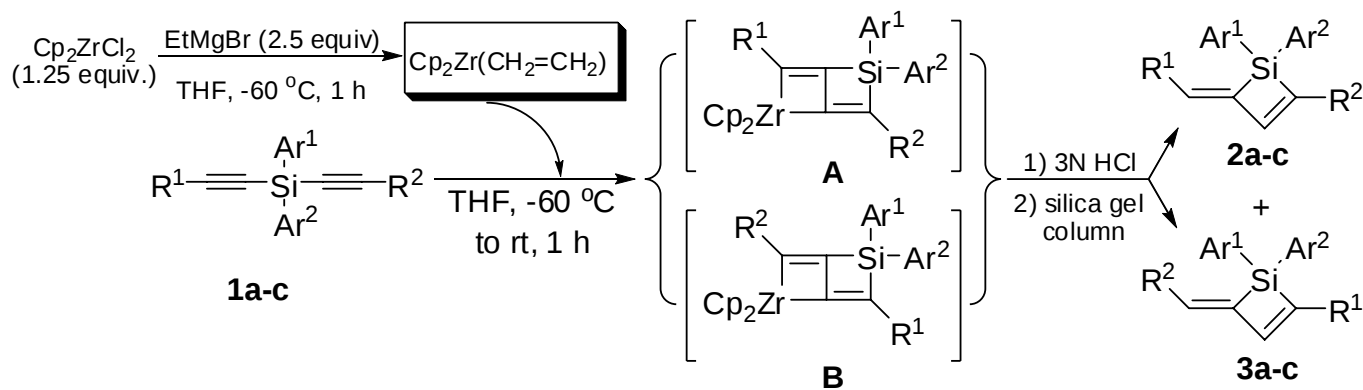
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Abstract – New types of silacyclobutene derivatives were synthesized by zirconocene- and titanocene-ethylene complexes-promoted reactions of some *rac*-dialkynyldiarylsilanes.

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 zirconacyclobutene intermediates (**A** and **B**), as shown in Scheme 1. Namely, a THF solution of zirconocene-ethylene complex Cp₂Zr(CH₂=CH₂), prepared *in situ* by reaction of Cp₂ZrCl₂ 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

† 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-CHCl₃ (10:1) (Table 1, Entry 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 ¹H NMR (400 MHz, CDCl₃) 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**).

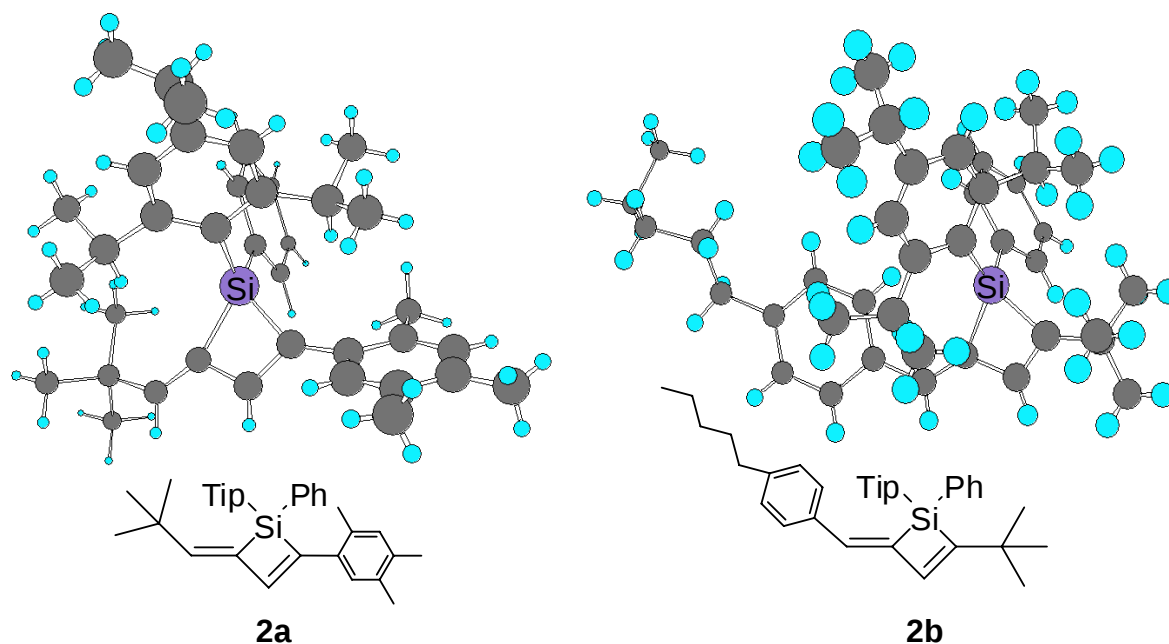


Figure 1. Computer-generated drawing derived from the X-Ray coordinates of compounds (**2a** and **2b**)

Tentative reactions of dialkynyldiarylsilanes (**1a,b**) with titanocene-ethylene complex $\text{Cp}_2\text{Ti}(\text{CH}_2=\text{CH}_2)$, prepared *in situ* by reaction of Cp_2TiCl_2 with EtMgBr in THF at $-60\text{ }^\circ\text{C}$, 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**: $J = 14.4\text{ Hz}$, **4b**: $J = 15.1\text{ Hz}$) were determined by their ^1H NMR analyses, HSQC and HMBC experiments.⁶ In the HMBC NMR spectrum of **4a**, the proton at $\delta\ 6.13$ ($\text{Si}-\underline{\text{CH}}=\text{CH}-$) ppm showed long-range correlations with carbon signals at $\delta\ 80.14$ ($\equiv\text{C}-\text{Si}$), 135.68 ($=\text{CH}-\underline{\text{Ph}}$), and 144.78 ($\text{Si}-\text{CH}=\underline{\text{CH}}$ -) ppm. In the case of **4b**, the proton at $\delta\ 6.12$ ($\text{Si}-\underline{\text{CH}}=\text{CH}-$) ppm showed long-range correlations with carbon signals at $\delta\ 80.37$ ($\equiv\text{C}-\text{Si}$), 136.14 ($=\text{CH}-\underline{\text{Ph}}$), and 146.04 ($\text{Si}-\text{CH}=\underline{\text{CH}}$ -) ppm. The different reaction mechanisms between zirconocene- and titanocene-complex-promoted reactions of **1a,b** are unclear.

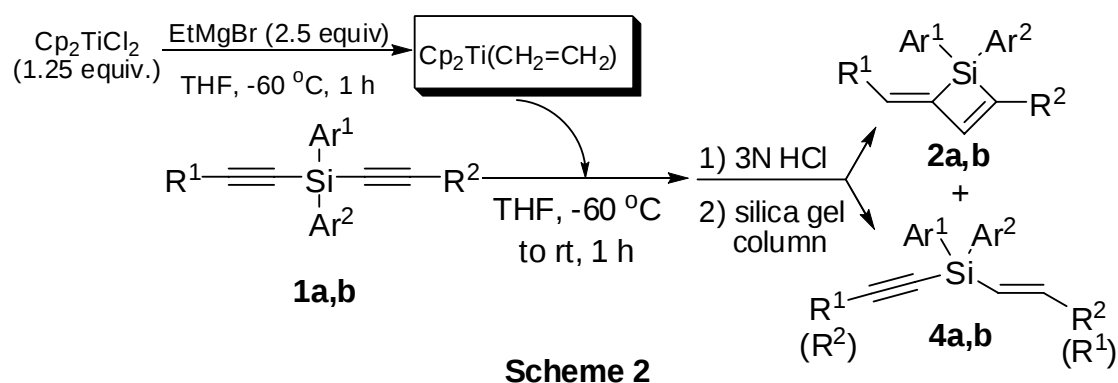
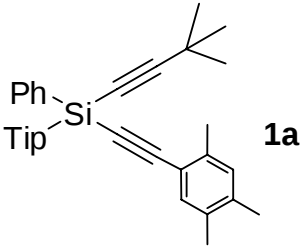
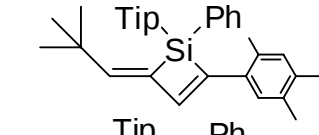
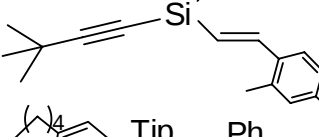
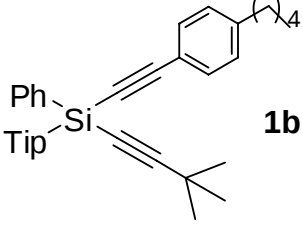
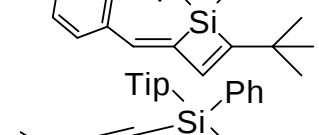


Table 2. Synthesis of Silacyclobutenes Utilizing Tirconocene - Ethylene Complex.

Entry	Dialkynyldiarylsilanes	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: C₃₈H₅₀Si. MW = 534.90, colorless block, monoclinic, space group P2₁/n(#14), a = 18.8910(7) Å, b = 8.6064(3) Å, c = 21.1085(6) Å, V = 3309.40(19) Å³, β = 105.3542(11)°, Z = 4, D_{calc} = 1.073 g/cm³, R = 0.0549, R_w = 0.1583; **2b**: C₄₀H₅₄Si. 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, D_{calc} = 1.062 g/cm³, R = 0.0825, R_w = 0.2421.
6. **4a**: ¹H NMR (400 MHz, CDCl₃) 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). ¹³C NMR (100MHz, CDCl₃) 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**: ¹H NMR (400 MHz, CDCl₃) 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). ¹³C NMR (100MHz, CDCl₃) 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.