Zirconocene Coupling Route to 1,2-Disilacyclobutanes

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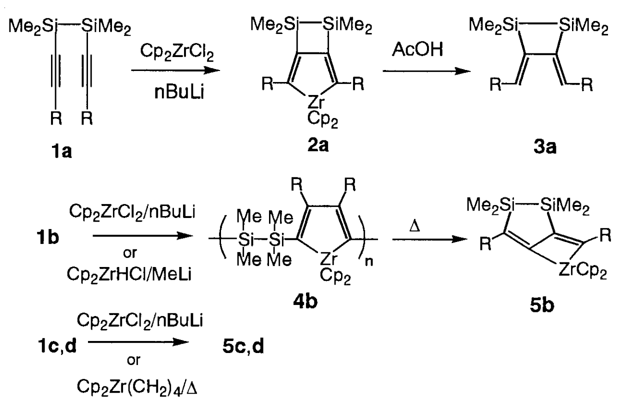
Zirconocene-mediated coupling of bis(methoxyethynyl)disilanes (**1a** and **1e**–**g**) led to zirconacycles (**2a** and **2e**–**g**), which were converted into 3,4-dialkylidene- and 3,4-benzo-1,2-disilacyclobutanes (**3a** and **6e**–**g**) via protonolysis and transmetallation with tin followed by Diels–Alder reaction. Their Si–Si bonds were reactive toward palladium catalyst to give bissilylation and silyl-Heck products (**8**, **9** and **10**).

1,2-Disilacyclobutanes showed spontaneous polymerization for ring opening polymerization (ROP) without solvent and catalysts as well as palladium-catalyzed Si–Si metathesis reaction.[1] It is a good candidate for monomers of silicon-based polymers.[1c,d] The zirconocene-induced bicyclization of diacetylene is a powerful new ring forming method,[2] which prompted us to investigate cyclization of bis(1,2-alkynyl)tetramethyldisilane (**1**).

The mode of reaction is highly dependent on the terminal substituents of **1**. Only when ethoxyethynyldisilane (**1a**) was treated with a zirconocene transfer reagent [$Cp_2Zr(n\text{-}Bu)_2$] (by addition of 2 equiv of *n*BuLi to Cp_2ZrCl_2 at –78 °C; Negishi's method[2a–c,f]), zirconabicycle (**2a**) bearing 1,2-disilacyclobutane framework was afforded quantitatively as shown in Scheme 1.

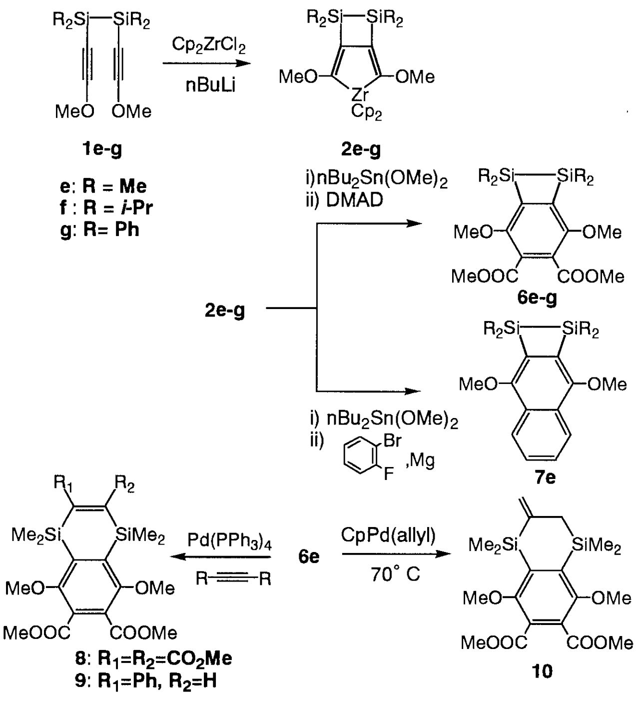
Scheme 1.



Successive protonolysis of **2a** with AcOH, 3,4-dialkylidene-1,2-disilacyclobutane **3a** was obtained as air-sensitive colorless oil in 78% yield.[3] It is noteworthy that **3a** showed strong tendency to undergo spontaneous ROP reaction, and only removal of solvent is enough to initiate polymerization and furnish a high molecular weight polymer (M_w=1.8 × 10^5, M_w/M_n=2.1). As compound **3a** also possesses 1,4-diethoxydiene moiety, Diels–Alder addition of activated dienophile with **3a** such as dimethyl acetylenedicarboxylate (DMAD), maleic anhydride, and maleimide smoothly proceeded at room temperature to give the corresponding adducts[3] in 32%, 57% and 56% yields, respectively.

On the contrary, in the case of 1,2-dipropynyldisilane (**1b**),[4a] both Negishi's reagent and hydrozirconation followed by methylation (Cp_2ZrHCl/MeLi)[5] resulted in the formation of black air-sensitive polymer (**4b**) in quantitative yield as shown in Scheme 1. The structure of **4b** was assigned to be a polymer containing a zirconacycle in the main chain based on spectroscopic resemblance with those for a model complex 2,5-bis(pentamethyldisilanyl)-3,4-dimethylzirconacyclopentadiene.[4a] Protonolysis of **4b** with CF_3CO_2H gave the corresponding colorless polymer of low molecular weight (M_w=5780, M_w/M_n=1.8) containing a dienyl group in the main chain. On the other hand, once the polymer (**4b**) was heated in THF, thermal depolymerization followed by intramolecular coupling with 1,2-migration of silyl group took place to give zirconacycle (**5b**) almost in quantitative yield. A similar depolymerization of zirconocene polymer has been applied to synthesize the macrocycles consisting of zirconacyclopentadienes,[2l–n] while a similar 1,2-silyl group migration finds a recent precedent in the intramolecular zirconocene coupling of bis(phenylethynyl)dimethylmonosilane.[2h,i] For trimethylsilyl and phenyl-substituted 1,2-dialkylidene disilanes (**1c** and **1d**), the reaction with Negishi's reagent at room temperature or modified reagent ($Cp_2Zr(CH_2)_4$) at 40 °C[6] underwent direct intramolecular coupling with 1,2-silyl group migration to give 1,2-disilacyclopen-

Scheme 2.



tanes (**5c** and **5d**) quantitatively.

With the increasing bulkiness of substituents on silicon atoms as can be seen for ^{i}Pr and Ph, bis(methoxyethynyl)disilanes (**1e–g**)[4b] were treated with Negishi's reagent to afford 1,2-disilacyclobutanes bearing zirconacycles (**2e**: 98% isolated yield and **2f** and **2g**: quantitative yields by NMR) as shown in Scheme 2. The conversion of readily prepared zirconacycles into the corresponding main-group heterocycles by Fagan–Nugent method has been shown to be extremely versatile.[7] In this work, the treatment of zirconacyclopentadienes (**2e–g**) with an equivalent of dibutyltin dimethoxide[7c,d] afforded the expected stannoles which were characterized by NMR. Without isolation, the stannoles were brought into contact with DMAD and with in situ generated benzyne to give new 3,4-benzo-1,2-disilacyclobutanes (**6e**: 56% isolated yield and **6f** and **6g**: quantitative yields by NMR) and 3,4-naphtho-1,2-disilacyclobutane (**7e**: 75% isolated yield) respectively.[3] Crystals of zirconacycle (**2f**) and 3,4-benzo-1,2-disilacyclobutane (**6e**) were successfully grown and their structures were confirmed by X-ray analyses (Figure 1).[8] Because two independent molecules of **2f** lie in a crystallographic two-fold axis, one of the molecules was shown in Figure 1. Intramolecular distance (3.42 Å) between oxygen and zirconium metal is too far to account any coordinative interaction. Owing to its steric bulkiness, the trimethylsilyl group is known to be located at α-position of zirconacyclopentadiene; [2a,5b] this reverse regiochemistry might be responsible for the electronic effect of alkoxy substituted silylacetylenes.

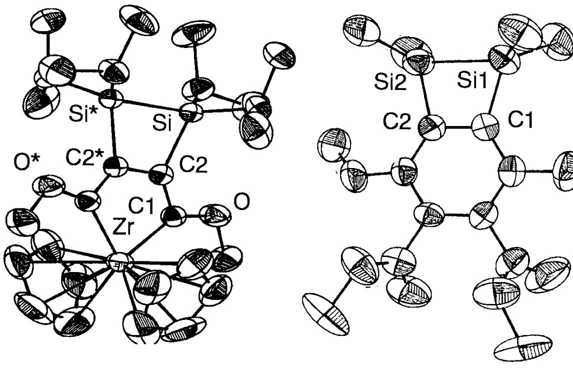


Figure 1. ORTEP drawing of **2f** (left) and **6e** (right). selected bondLength (Å) and angles (°) of **2f**: Si-Si* 2.364(8), Si-C(2) 1.893(6), C(2)-C(2)* 1.559(9), Si*-Si-C(2) 77.2, Si-C(2)-C(2)* 101.6. selected bondLength (Å) and Angles (°) of **6e**: Si(1)-Si(2) 2.320(2), Si(1)-C(1) 1.882(5), Si(2)-C(2) 1.897(6), C(1)-C(2) 1.413(7), Si(2)-Si(1)-C(1) 75.7(2), Si(1)-Si(2)-C(2) 76.4(2), Si(1)-C(1)-C(2) 104.9(4), Si(2)-C(2)-C(1) 102.6(4).

The stoichiometric reactions of 3,4-benzo-1,2-disilacyclobutane (**6e**) with $Pd(PPh_3)_4$ and $Pd(CN^tBu)_2$ resulted in no Si–Si metathesis reaction. Instead, the quantitative formation of the corresponding bissilylpalladium complexes ($L_2Pd[\eta^2$-1,2-$(SiMe_2)_2Ar]$: L=Ph_3P or CN^tBu) took place as intermediates showing characteristic low field ^{29}Si-NMR signals at 31.2 ppm and 39.6 ppm, respectively. Successive addition of acetylenes gave bissilylation products (**8** and **9**: 90% yield), which were also produced catalytically as shown in Scheme 2. Meanwhile, intramolecular silyl-Heck type reaction (from **6e** to **10**) took place in a stoichiometric reaction of **6e** with CpPd(Allyl) in 32% isolated yield.

Summarizing our attempts, we demonstrated that zirconocene mediated small-ring formations were effected depending on terminal substituents of diyne, and the zirconacycles obtained in this route were converted into a variety of types of 1,2-disilacyclobutanes.

References and Notes

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3 All new products obtained here showed satisfactory spectral data.

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8 Suitable crystals were obtained by recrystallization from hexane in a glove box. Crystal data of **2f**: $C_{28}H_{44}Si_2ZrO_2$, M=560.05, monoclinic with a=14.809(7), b=11.768(2), c=17.568(5) Å, β=106.48(3)°, V=2935.9 Å^3, space group *P2/c* Z=4, d_{calcd}=1.27 g/cm^3, μ(Mo Kα)=4.7 cm^{-1}. Crystal data for **6e**: $C_{16}H_{24}Si_2O_6$, M=364.54, monoclinic with a=6.767(1) Å, b=19.273(2) Å, c=15.776(1) Å, β=95.47(1)°, V=2048.0 Å^3, space group *P21/n*, Z=4, μ(Mo Kα)=1.9 cm^{-1}, d_{calcd}=1.19 g/cm^3. The 5607 and 1812 independent reflections [$2\theta \leq 50°$; $|Fo^2| > 3\sigma|Fo^2|$] were measured on an Enraf–Nonius CAD4 diffractometer using Mo Kα radiation and ω-2θ scan. The structures were solved by direct methods and all non-hydrogen atoms were refined anisotropically to R=0.066 and R=0.055 (Rw=0.079 and Rw=0.059), respectively .