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Reactions of bis(alkynyl)silanes with $HB(C_6F_5)_2$: Formation of boryl-substituted silacyclobutene derivatives

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ABSTRACT

Treatment of $R_2Si(C{\equiv}C\text{-}SiMe_3)_2$ [**1a** (Me), **1b** (Ph)] with $HB(C_6F_5)_2$ at low temperature (253 K (**a**), 273 K (**b**)) gives the $-B(C_6F_5)_2$ substituted silacyclobutene products (**4a**,**b**) under kinetic control. Upon warming to room temperature they disappear to form the thermodynamically favoured isomeric silole derivatives (**2a**,**b**). Similar treatment of $Me_2Si(C{\equiv}C{-}R^1)_2$ [**5a** (R^1 = Ph), **5b** (R^1 = tert-butyl) with $HB(C_6F_5)_2$ at room temperature gave the stable $-B(C_6F_5)_2$ substituted silacyclobutene derivatives **6** and **7**, respectively. Subsequent photolysis resulted in a *Z*- to *E*-isomerization of the substituted exocyclic C=C double bonds in these products. The silacyclobutene derivative *E*-**6** was characterized by an X-ray crystal structure analysis.

1. Introduction

We had recently shown that the bis(trimethylsilylethynyl) silanes **1a** ($R = CH_3$) and **1b** (R = Ph) reacted readily with Piers' borane [$HB(C_6F_5)_2$] at room temperature to yield the $-B(C_6F_5)_2$ substituted silole derivatives **2a** and **2b**, respectively (see Chart 1) [1]. These products are probably formed by means of a reaction sequence formally involving a 1,1-hydroboration followed by 1,1-vinylboration after a subsequent alkynyl shift from silicon to boron, similarly as it was previously proposed by Wrackmeyer et al. for many related examples employing less electrophilic boranes [2,3]. We could then show that the silole derivatives **2a**,**b** undergo a clean rearrangement reaction to yield the isomeric products **3a**,**b** upon photolysis (HPK 125, Pyrex filter). This photoreaction follows a pattern reminiscent of the di-π-methane rearrangement [4]. We have now found that the formation of the silole derivatives **2a**,**b** is preceded by the formation of their boryl-substituted silacyclobutene isomers which can be observed when the reaction of the bis(alkynyl)silanes (**1a**,**b**) with $HB(C_6F_5)_2$ is performed under kinetic control at low temperatures. We have also found that formation of stable silacyclobutene derivatives can become dominant in the reaction of differently substituted bis(alkynyl)silanes with $HB(C_6F_5)_2$. We will describe several such examples in this account.

2. Results and discussion

Bis(trimethylsilylethynyl)dimethylsilane **1a** [1.3b] was mixed with 1 M equivalent of $HB(C_6F_5)_2$ [5] in d_8-toluene at −78 °C. The sample was sealed in an NMR tube. The reaction mixture was then slowly warmed to −20 °C and the progress of the reaction was monitored by NMR spectroscopy. The NMR spectra show the formation of the silacyclobutene derivative **4a** under kinetic control. The assignment was supported by the NMR analysis of the system (for details see the Supporting information), and its comparison with the data of the isomers **2a** and **3a** and a comparison with a differently substituted analogous borylsilacyclobutene derivative [6] that was characterized by X-ray diffraction (see below) (Scheme 1).

The $-B(C_6F_5)_2$ substituted silacyclobutene product **4a** features a set of four ^{13}C NMR resonances of the core at δ 188.6 (br, C3), 173.6 (br, C2), 168.4 ($^1J_{Si,C}$ = 52.1 Hz, C4) and 131.5 ($^1J_{Si,C}$ = 68.1 Hz, C5) that are distinctly different from those of both silole isomers **2a** [δ 174.2 (br, C3), 159.8 (C2), 150.9 (C4) and 149.9 (C5) in d_6-benzene] and **3a** [δ 171.5 ($^1J_{Si,C}$ = 61.7 Hz, C3), 181.1 ($^1J_{Si,C}$ = 58.3 Hz, $^1J_{Si,C}$ = 42.2 Hz, C2), 172.1 (C4) and 151.6 (br, C5)]. Compound **4a** shows the ^1H NMR signal of the olefinic 5-H proton at δ 5.94 with a coupling constant of $^3J_{Si,H}$ = 22.1 Hz and $^2J_{Si,H}$ = 5.3 Hz (298 K), respectively [cf. **2a**: δ 7.42 ($^3J_{Si,H}$ = 16.9 Hz and 7.5 Hz)]. Compound **4a** shows three ^{29}Si NMR signals [δ −7.7 (5-Si), −11.1 (2-Si) and 21.8 ($SiMe_2$); cf. **2a**: δ −7.1, −9.6, 25.6]. The ^{11}B NMR signal of compound **4a** is broad ($\nu_{1/2}$ ≈ 2500 Hz) and occurs at δ 64 and the ^{19}F NMR

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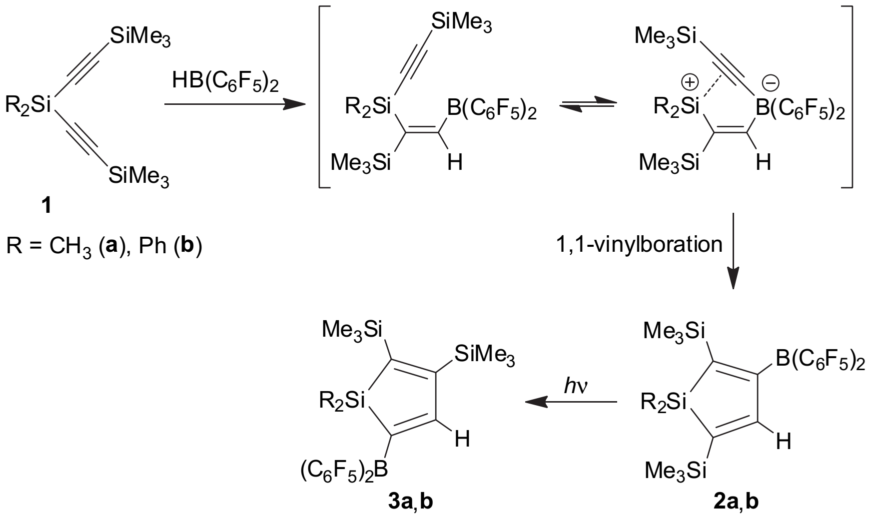


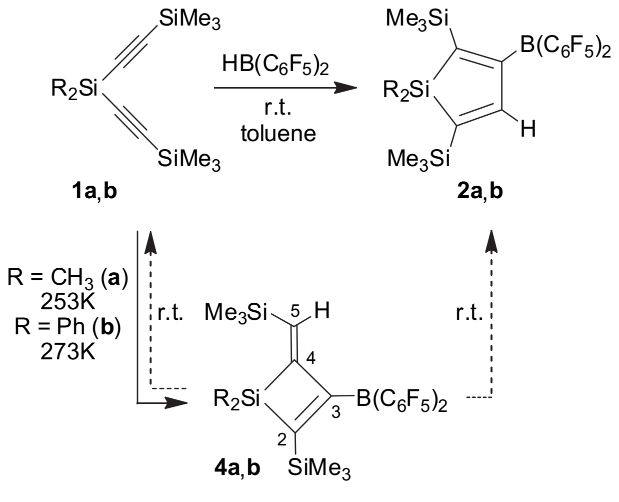
Chart 1.

resonances are located at δ −126.9 (o), −143.2 (p) and −160.7 (m). Both the chemical shift of the ^{11}B and the observed large ^{19}F NMR $\Delta\delta$(p, m) shift difference (17.5 ppm) of the C_6F_5 groups at boron are typical of a Lewis acidic tricoordinate boron.

The corresponding bis(trimethylsilylethynyl)diphenylsilane starting material (**1b**) reacts analogously with $HB(C_6F_5)_2$ under kinetic control. In this case we can warm the *in situ* prepared sample to 0 °C to observe the formation of the respective borylsilacyclobutene derivative **4b**, which was characterized spectroscopically (for details see the Experimental section).

Upon warming the samples containing either **4a** or **4b** to room temperature their characteristic NMR signals disappear and we observed the formation of the previously characterized boryl-silole derivatives **2a** and **2b**, respectively [1].

Changing the substituents at the alkynyl groups of the starting materials allowed us to shift the reaction course completely to the formation of stable $-B(C_6F_5)_2$ substituted silacyclobutene products [7]. We reacted bis(phenylethynyl)dimethylsilane (**5a**) with $HB(C_6F_5)_2$ in toluene. After 1 day at room temperature a 2: 1 mixture of the products *Z*-**6** and *E*-**6** was isolated in a combined yield of 89%. We obtained single crystals of the minor isomer *E*-**6** from the mixture by crystallization from pentane at −30 °C.



Scheme 1.

The X-ray crystal structure analysis (see Fig. 1) confirms the formation of the four-membered heterocyclic product. The silacyclobutene type core structure contains three sp^2-hybridized carbon atoms. The C2–C3 linkage (1.362(4) Å) is in the typical C=C double bond range. The C3–C4 C(sp^2)-C(sp^2) single bond is much longer (1.495(4) Å) and the exocyclic C4–C5 carbon–carbon double bond is again short (1.334(4) Å). The central C_3Si four-membered ring unit has a “kite shaped” structure. The Si1–C2 (1.883(3) Å) and Si1–C4 (1.862(3) Å) vectors comprise an internal bonding angle of 74.6(1)° (i.e. C2–Si1–C4). Consequently the external C11–Si1–C12 angle is much larger (111.6(2)°). The remaining angles inside the central C_3Si heterocycle were found at 105.1(2)° (C2–C3–C4), 88.5 (2)° (C3–C4–Si1) and 91.7(2)° (C3–C2–Si1).

The phenyl substituent at C5 is found trans-oriented to silicon at the exocyclic C4 = C5 carbon–carbon double bond, which denotes the product as the *E*-**6** isomer. The plane of the 5-phenyl

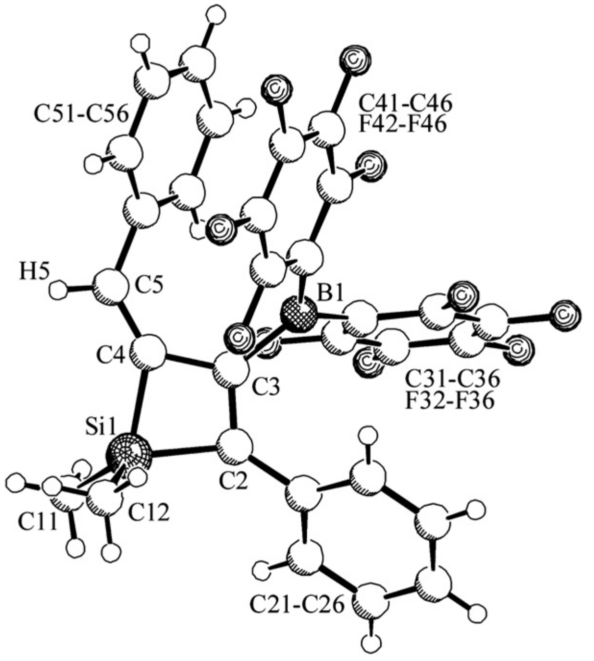


Fig. 1. Molecular structure of compound *E*-**6**.

Table 1
Selected NMR data of the $-B(C_6F_5)_2$ substituted silacyclobutene derivatives **6** and **7**.[a]

	E-**6**	*Z*-**6**	*E*-**7**	*Z*-**7**
	^{13}C NMR			
C2	172.4	168.8	181.0	176.8
C3 (br)	170.9	172.0	164.0	166.4
C4	149.9	149.1	139.7	143.4
C5	127.8	129.9	136.0	140.9
	^{1}H NMR			
5-H	6.53	6.72	5.36	5.47
	^{29}Si NMR			
Si1	14.2	13.8	15.9	11.2
	^{11}B NMR			
B1	58	65	–	64
	^{19}F NMR			
o-F	−126.7	−127.8	−125.6	−127.6
p-F	−146.2	−143.5	−144.6	−144.8
m-F	−162.1	−160.7	−161.4	−161.1

[a] NMR spectra in d_6-benzene at 298 K.

substituent is markedly rotated away from the adjacent olefinic plane. The second phenyl substituent is found attached at the ring carbon C2. This phenyl group is rotated out of the plane of the central four-membered heterocyclic core. The $-B(C_6F_5)_2$ substituent is attached at C3 (C3–B1: 1.554(4) Å). The boron atom in compound *E*-**6** is trigonal planar (sum of C–B–C angles: 360.1(3)°). The plane of one of the C_6F_5 rings (C41–C46) at the boron and the phenyl substituent at C5 (C51–C56) are oriented close to parallel (distance between the centroids of theses two rings: 3.411 Å). This may possibly indicate the presence of a π,π-stacking interaction between these units [8].

Compounds *E*-**6** and *Z*-**6** show very typical NMR data (see Table 1). They both feature ^{11}B NMR signals in the typical $R-B(C_6F_5)_2$ tricoordinate boron range [9]. Consequently, the corresponding ^{19}F NMR spectra show large $\Delta\delta$(p,m) [16.6 ± 0.7] differences [10]. Both isomers show similar ^{13}C NMR and ^{29}Si NMR values of the central C_3Si core (see Table 1) [6]. Photolysis of the initially formed *Z*-**6**/*E*-**6** mixture (HPK 125, toluene, r.t., 2 h) with UV light leads to a rather efficient *Z*-**6** to *E*-**6** isomerization. We have isolated a product in 75% yield that consists of the almost pure *E*-**6** isomer (*E*-**6**/*Z*-**6** ≈ 10:1).

The reaction of bis(3,3-dimethyl-1-butynyl)dimethylsilane (**5b**) with $HB(C_6F_5)_2$ in toluene at room temperature (overnight) gave a 78% yield of the $-B(C_6F_5)_2$ substituted silacyclobutene derivative *Z*-**7** (see Scheme 2, see Table 1 for the NMR data). Photolysis of the pure *Z*-**7** isomer (toluene, 2 h, r.t.) resulted in *Z*-**7**–*E*-**7** isomerization. From the workup procedure we isolated an *E*-**7**/*Z*-**7** product mixture of ca. 3.5:1. The spectroscopic characterization of the major component, the photoproduct *E*-**7**, was carried out from this product mixture (see Table 1). We note that all the compounds **6** and **7** have very similar characteristic NMR spectroscopic parameters.

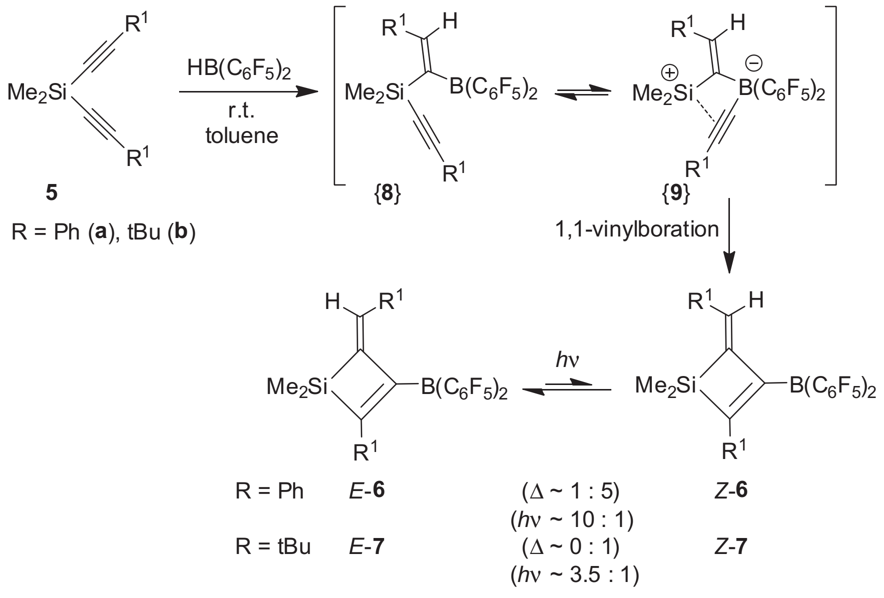
The borylsilacyclobutene product formation by treatment of the substituted bis(alkynyl)silane starting materials with Piers' borane can be rationalized along the lines as previously proposed by Wrackmeyer et al. for the analogous four-membered ring product formation of bis(alkynyl)silanes with BR_3 reagents [2,6]. In our case we propose initial 1,2-hydroboration which would lead to the intermediate {**8**} (see Scheme 2) followed by intermolecular alkynyl-transfer from silicon to boron. Subsequent 1,1-vinylboration at the state of {**9**} would then lead to the observed four-membered ring products [6].

This work shows that reactions of alkynes with main-group metal substituents with suitable $R-B(C_6F_5)_2$ reagents [here $HB(C_6F_5)_2$] principally follows some of the reaction pathways that were established or proposed to proceed with the "classical" R_3B trialkylborane reagents, only that the special C_6F_5 substituted borane reagents seem to often undergo such reactions much more easily and under very mild reaction conditions.

3. Experimental section

3.1. General information

Reactions with air- and moisture-sensitive compounds were carried out under an argon atmosphere using Schlenk-type glassware or a glove-box. Solvents were dried with the procedure reported by *Grubbs* [11] or, particularly deuterated solvents, were distilled from appropriate drying agents and stored under an argon atmosphere. The following instruments were used for physical characterization of the compounds: NMR: Varian Inova 500 (^1H: 500 MHz, $\delta^1H(TMS) = 0$; ^{11}B: 161 MHz, $\delta^{11}B(BF_3 \times OEt_2) = 0$; ^{13}C: 126 MHz, $\delta^{13}C(TMS) = 0$; ^{19}F: 470 MHz, $\delta^{19}F(CFCl_3) = 0$; ^{29}Si: 99 MHz {using DEPT pulse sequence based on $J_{Si,H} = 7.0$ Hz}, $\delta^{29}Si$



Scheme 2.

(TMS) = 0). Most NMR assignments were supported by additional 2D experiments. The IR spectra were obtained with a Varian 3100 FT-IR (EXCALIBUR Series) spectrometer, the MS GC-EI with Triple-quad TSQ (Thermo-Finnigan-MAT, Bremen). Elemental analyses were performed with a Foss-Heraeus CHN-O-Rapid instrument.

Data set was collected with a Nonius KappaCCD diffractometer, equipped with a rotating anode generator. Programs used: data collection COLLECT (Nonius B.V., **1998**), data reduction Denzo-SMN [12], absorption correction Denzo [13], structure solution SHELXS-97 [14], structure refinement SHELXL-97 [15], graphics SCHAKAL (E. Keller, Univ. Freiburg, **1997**).

3.1.1. NMR-scale determination of the intermediate of Z-*4a* and Z-*4b*

***Z*-4a**: Bis(trimethylsilylethynyl)dimethylsilane (**1a**) (20.0 mg, 0.08 mmol), and bis(pentafluorophenyl)borane (27.4 mg, 0.08 mmol) were weighed in an argon-filled glove-box and put inside an NMR tube. The tube was then cooled to −78 °C and d_8-toluene (0.8 mL) was added by a syringe under argon. The tube was then sealed under vacuum and kept at low temperature until the measurement, performed at −20 °C in a pre-cooled NMR spectrometer.

^{1}H NMR (C_7D_8, 253 K): δ 5.94 (s, $J_{Si,H} = 22.1$ Hz, 1H, 5-H), 0.42 (s, 6 H, $SiMe_2$), 0.03 (s, 9 H, 5-$SiMe_3$), −0.11 (s, 9 H, 2-$SiMe_3$). ^{13}C{^{1}H} NMR (C_7D_8, 253 K): δ 188.6 (br, C3), 173.6 (br, C2), 168.4 ($^{1}J_{Si,C} = 52.1$ Hz, C4), 148.8 (dm, $^{1}J_{F,C} \approx 254$ Hz, C_6F_5), 144.7 (dm, $^{1}J_{F,C} \approx 263$ Hz, C_6F_5), 137.6 (dm, $^{1}J_{F,C} \approx 253$ Hz, C_6F_5), 131.5 ($^{1}J_{Si,C} = 68.1$ Hz, C5), 113.6 (br, *i*-C_6F_5), 0.4 ($^{1}J_{Si,C} = 44.7$ Hz, $SiMe_2$), −0.3 ($^{1}J_{Si,C} = 51.8$ Hz, 2-$SiMe_3$), −0.6 ($^{1}J_{Si,C} = 52.1$ Hz, 5-$SiMe_3$). ^{11}B{^{1}H} NMR (C_7D_8, 243 K): δ 64 ($\nu_{1/2} \approx 2500$ Hz). ^{19}F NMR (C_7D_8, 253 K): δ −126.9 (m, 2 F, *o*-F), −143.2 (t, $^{3}J_{F,F} = 20.8$ Hz, 1 F, *p*-F), −160.7 (m, 2 F, *m*-F) [$\Delta\delta_{m,p} = 17.5$]. ^{29}Si{^{1}H} NMR ($C_7D_8$, 253 K): δ 21.8 ($SiMe_2$), −7.7 (5-Si), −11.1 (2-Si).

***Z*-4b**: Bis(trimethylsilylethynyl)diphenylsilane (**1b**) (25.0 mg, 0.07 mmol), and bis(pentafluorophenyl)borane (22.6 mg, 0.07 mmol) were weighed under argon and placed inside an NMR tube. The tube was then cooled to −78 °C and d_8-toluene (0.8 mL) was added by a syringe. The tube was then sealed under vacuum and kept at low temperature until the measurement, performed at 0 °C in a pre-cooled NMR instrumentation.

^{1}H NMR (C_7D_8, 273 K): δ 7.88 (m, 4 H, *o*-Ph), 7.19 (m, 4 H, *m*-Ph), 7.13 (m, 2 H, *p*-Ph), 6.13 (s, $J_{Si,H} = 23.1$ Hz, 5-H), −0.11 (s, $^{2}J_{Si,H} = 6.5$ Hz, 9 H, 5-$SiMe_3$), −0.18 (s, $^{2}J_{Si,H} = 6.6$ Hz, 9 H, 2-$SiMe_3$). ^{13}C{^{1}H} NMR (C_7D_8, 273 K): δ 193.9 (br, C3), 174.2 (br, C2), 166.2 (C4), 148.9 (dm, $^{1}J_{F,C} \approx 253$ Hz, C_6F_5), 145.0 (dm, $^{1}J_{F,C}$~262 Hz, C_6F_5), 137.7 (dm, $^{1}J_{F,C} \approx 254$ Hz, C_6F_5), 135.9 (*o*-Ph), 133.8 ($^{1}J_{Si,C} = 63.5$ Hz, *i*-Ph), 132.7 ($^{1}J_{Si,C} = 65.5$ Hz, C5), 130.9 (*p*-Ph), 128.5 (*m*-Ph), 113.7 (br, *i*-C_6F_5), −0.1 (2-$SiMe_3$), −0.7 (5-$SiMe_3$). ^{11}B{^{1}H} NMR (C_7D_8, 273 K): δ 64 (br, ν½ ≈ 2400 Hz). ^{19}F NMR (C_7D_8, 273 K): δ −126.5 (m, 2 F, *o*-F), −143.1 (m, 1 F, *p*-F), −160.6 (m, 2 F, *m*-F) [$\Delta\delta_{m,p} = 17.5$]. ^{29}Si{DEPT} NMR ($C_7D_8$, 273 K): δ 7.9 ($SiPh_2$), −6.5 (5-Si), −10.7 (2-Si).

3.1.2. 3-Bis(pentafluorophenyl)boryl-2-phenyl-4-benzylidene-dimethylsilacyclobut-2-ene (Z-*6*, E-*6*)

Representative experiment: Bis(phenylethynyl)dimethylsilane (**5a**) (400 mg, 1.54 mmol), and bis(pentafluorophenyl)borane (531 mg, 1.54 mmol), were weighed in an argon-filled glove-box and put into a Schlenk flask (200 mL). Toluene (50 mL) was added by cannula under argon and the resulting bright red solution was stirred overnight. The day after, the volatiles were removed under high vacuum leaving a yellow oily product that was washed with pentane (1 × 20 mL). A yellow powder was obtained after removing the volatiles by high vacuum. Yield 89% (825 mg). The NMR spectra showed the presence of both *Z*-**6** and *E*-**6** isomers (here: *Z*: *E* ≈ 5: 1). Crystals of the *E* isomer suitable for X-ray diffraction were obtained from a concentrated pentane solution at −30 °C.

***Z*-6**: ^{1}H NMR (C_6D_6, 298 K): δ 7.28 (m, 2 H, *o*-Ph^{5}), 7.11 (m, 2 H, *m*-Ph^{5}), 7.04 (m, 4 H, *o*, *m*-Ph^{2}), 7.02 (m, 1 H, *p*-Ph^{5}) 6.91 (m, 1 H, *p*-Ph^{2}) 6.90 (m, 2 H, *p*-Ph^{2}), 6.72 (s, $^{3}J_{Si,H} = 16.3$ Hz, 1 H, 5-H), 0.54 (s, $^{2}J_{Si,H} = 6.8$ Hz, 6 H, $SiMe_2$). ^{13}C{^{1}H} NMR (C_6D_6, 298 K): δ 172.0 (br, C3), 168.8 ($^{1}J_{Si,C} = 53.8$ Hz, C2), 149.1 ($^{1}J_{Si,C} = 52.9$ Hz, C4), 147.8 (dm, $^{1}J_{F,C} \approx 254$ Hz, C_6F_5), 144.7 (dm, $^{1}J_{F,C} \approx 261$ Hz, C_6F_5), 139.6 (*i*-Ph^{5}), 138.7 (*i*-Ph^{2}), 137.7 (dm, $^{1}J_{F,C} \approx 253$ Hz, C_6F_5), 129.9 ($^{1}J_{Si,C} = 66.6$ Hz, C5), 129.0 (*m*-Ph^{5}), 128.9 (*o*-Ph^{2}), 128.5 (*m*-Ph^{2}), 128.4 (*p*-Ph^{2}), 127.5 (*p*-Ph^{5}), 126.5 (*o*-Ph^{5}), 113.3 (br, *i*-C_6F_5), −0.8 ($^{1}J_{Si,C} = 47.3$ Hz, $SiMe_2$). ^{11}B{^{1}H} NMR (C_6D_6, 298 K): δ 65 (br, ν½ ≈ 1900 Hz). ^{19}F NMR (C_6D_6, 298 K): δ −127.8 (m, 2 F, *o*-F), −143.5 (tt, $^{3}J_{F,F} = 20.7$ Hz, $^{4}J_{F,F} = 6.4$ Hz, 2 F, *p*-F), −160.7 (m, 4 F, *m*-F) [$\Delta\delta_{m,p} = 17.2$]. ^{29}Si {DEPT} NMR ($C_6D_6$, 298 K): δ 13.8 ($SiMe_2$).

***E*-6**: ^{1}H NMR (C_6D_6, 298 K): δ 7.01 (m, 4 H, *o*-Ph^{5}), 6.94 (m, 2 H, *m*-Ph^{2}) 6.90 (m, 2 H, *o*-Ph^{2}), 6.82 (m, 4 H, *p*-Ph^{2}), 6.81 (m, 4 H, *m*-Ph^{5}), 6.79 (m, 1 H, *p*-Ph^{5}), 6.53 (s, $^{3}J_{Si,H} = 9.6$ Hz, H, 5-H), 0.44 (s, $^{2}J_{Si,H} = 6.9$ Hz, 6 H, $SiMe_2$). ^{13}C{^{1}H} NMR (C_6D_6, 298 K): δ 172.4 (C2), 170.9 (br, C3), 149.9 (C4), 148.8 (dm, $^{1}J_{F,C} \approx 252$ Hz, C_6F_5), 143.9 (dm, $^{1}J_{F,C} \approx 260$ Hz, C_6F_5), 143.5 (*i*-Ph^{5}), 139.3 (*i*-Ph^{2}), 137.5 (dm, $^{1}J_{F,C} \approx 251$ Hz, C_6F_5), 129.7 (*m*-Ph^{5}), 128.4 (*m*-Ph^{2}), 127.9 (*p*-Ph^{2}), 127.8 (C5), 127.7 (*o*-Ph^{2}), 126.7 (*p*-Ph^{5}), 126.3 (*o*-Ph^{5}), 113.4 (br, *i*-C_6F_5), −1.8 ($^{1}J_{Si,C} = 47.0$ Hz, $SiMe_2$). ^{11}B{^{1}H} NMR (C_6D_6, 298 K): δ 58 (br, ν½ ≈ 2100 Hz). ^{19}F NMR (C_6D_6, 298 K): δ −126.7 (br m, 2 F, *o*-F), −146.2 (tt, $^{3}J_{F,F} = 20.7$ Hz, $^{4}J_{F,F} = 6.2$ Hz, 1 F, *p*-F), −162.1 (br, 2 F, *m*-F) [$\Delta\delta_{m,p} = 15.9$]. ^{29}Si{^{1}H} NMR ($C_6D_6$, 298 K): δ 14.2 ($SiMe_2$).

X-ray crystal structure analysis of ***E*-6**: formula $C_{30}H_{17}BF_{10}Si$, $M = 606.34$, yellow crystal 0.35 × 0.30 × 0.15 mm, $a = 19.0604(3)$, $b = 7.1624(2)$, $c = 22.4928(5)$ Å, $\beta = 115.392(1)$o, $V = 2774.03(11)$ Å^{3}, $\rho_{calc} = 1.452$ g cm^{-3}, $\mu = 0.171$ mm^{-1}, empirical absorption correction ($0.942 \le T \le 0.975$), $Z = 4$, monoclinic, space group $P2_1/c$ (No. 14), $\lambda = 0.71073$ Å, $T = 223(2)$ K, ω and φ scans, 23002 reflections collected ($\pm h$, $\pm k$, $\pm l$), $[(\sin\theta)/\lambda] = 0.67$ Å^{-1}, 6516 independent ($R_{int} = 0.054$) and 4399 observed reflections [$I \ge 2\ \sigma(I)$], 381 refined parameters, $R = 0.069$, $wR^2 = 0.149$, max. (min.) residual electron density 0.20 (−0.28) e Å^{-3}, hydrogen atoms calculated and refined as riding atoms.

3.1.3. Irradiation of *E-6/Z-6*

Bis(phenylethynyl)dimethylsilane (**5a**) (300 mg, 1.15 mmol), and bis(pentafluorophenyl)-borane (398 mg, 1.15 mmol), were weighed in an argon-filled glove-box into a Schlenk flask (200 mL). Toluene (30 mL) was added, and the bright red solution was stirred for 4 h. After this time, the solution was irradiated with UV lamp for 2 h with stirring at room temperature. After irradiation the colour of the solution was still red but darker than before. The volatiles were then removed and the product was washed with hexane (2 × 20 mL). A dark-red powder was obtained with yield 75% (525 mg). The two isomers were present in photochemical equilibrium of ***E*-6**: ***Z*-6** ≈ 10: 1, which did not change after several days at environmental light. For NMR characterization, see above.

3.1.4. 3-Bis(pentafluorophenyl)boryl-2-(1,1-dimethylethyl)-4-(Z)-(2,2-dimethylpropylidene)-dimethylsilacyclobut-2-ene (Z-*7*)

Bis(3,3-dimethyl-1-butynyl)dimethylsilane (**5b**) (400 mg, 1.81 mmol), and bis(pentafluorophenyl)borane (628 mg, 1.81 mmol), were weighed in an argon-filled glove-box and put into a Schlenk flask (100 mL). Toluene (30 mL) was added by cannula under argon and the resulting bright yellow solution was stirred overnight. The day after, the volatiles were removed under high vacuum leaving a yellow oil. The product was washed with pentane (1 × 50 mL), and no further purification was performed. Yield 78% (805 mg).

^{1}H NMR (C_6D_6, 298 K): δ 5.47 (s, $^{3}J_{Si,H} = 17.2$ Hz, 1H, 5-H), 0.97 (s, 9 H, 2-$C(CH_3)_3$), 0.93 (s, 9 H, 5-$C(CH_3)_3$), 0.44 (s, $^{2}J_{Si,H} = 6.9$ Hz, 6 H,

$SiMe_2$). $^{13}C\{^1H\}$ NMR (C_6D_6, 298 K): δ 176.8 ($^1J_{Si,C} = 53.2$ Hz, C2), 166.4 (br, C3), 148.6 (dm, $^1J_{F,C} \approx 252$ Hz, C_6F_5), 144.6 (dm, $^1J_{F,C} \approx 261$ Hz, C_6F_5), 143.4 (C4), 140.9 (C5), 137.7 (dm, $^1J_{F,C} \approx 253$ Hz, C_6F_5), 114.4 (br, *i*-C_6F_5), 36.1 (C_{quat}, 2-$C(CH_3)_3$), 34.7 (C_{quat}, 5-$C(CH_3)_3$), 31.0 (2-$C(CH_3)_3$), 30.0 (5-$C(CH_3)_3$), 0.6 ($^1J_{Si,C} = 46.3$ Hz, $SiMe_2$). $^{11}B\{^1H\}$ NMR (C_6D_6, 298 K): δ 64 (br, $\nu½ \approx 1500$ Hz). ^{19}F NMR (C_6D_6, 298 K): δ −127.6 (m, 2 F, *o*-F), −144.8 (tt, $^3J_{F,F} = 20.9$ Hz, $^4J_{F,F} = 5.9$ Hz, 1 F, *p*-F), −161.1 (m, 2 F, *m*-F) [$\Delta\delta_{m,p} = 16.3$]. $^{29}Si\{^1H\}$ NMR (C_6D_6, 298 K): δ 11.2 ($SiMe_2$).

*3.1.4.1. Irradiation of **Z-7**: preparation of **E-7**.* 3-Bis(pentafluorophenyl)boryl-2-(1,1-dimethylethyl)-4-(*Z*)-(2,2-dimethylpropylidene)-dimethylsilacyclobut-2-ene (***Z*-7**) (420 mg, 0.741 mmol) was dissolved by toluene (10 mL) in a Schlenk flask (50 mL) under argon with stirring, and the bright yellow solution was irradiated with UV lamp for 2 h. The volatiles were then removed and the product was washed by pentane (2 × 10 mL). The isomer E-**7** was formed in photochemical equilibrium of *E*-**7**: *Z*-**7**~3.5: 1, which did not change after several days at environmental light. Isolated yield for the isomers mixture 68% (285 mg).

^1H NMR (C_6D_6, 298 K): δ 5.36 (s, $^3J_{Si,H} = 13.8$ Hz, 1 H, 5-H), 0.90 (s, 9 H, 2-$C(CH_3)_3$), 0.81 (s, 9 H, 5-$C(CH_3)_3$), 0.37 (s, $^2J_{Si,H} = 6.9$ Hz, 6 H, $SiMe_2$). $^{13}C\{^1H\}$ NMR (C_6D_6, 298 K): δ 181.0 ($^1J_{Si,C} = 50.3$ Hz, C2), 164.0 (br, C3), 149.5 (dm, $^1J_{F,C} \approx 253$ Hz, C_6F_5), 144.7 (dm, $^1J_{F,C} \approx 261$ Hz, C_6F_5), 139.7 ($^1J_{Si,C} = 55.2$ Hz, C4), 137.8 (dm, $^1J_{F,C} \approx 252$ Hz, C_6F_5), 136.0 (C5), 114.4 (br, *i*-C_6F_5), 36.1 (C_{quat}, 2-$C(CH_3)_3$), 32.7 (C_{quat}, 5-$C(CH_3)_3$), 31.6 (2-$C(CH_3)_3$), 30.3 (5-$C(CH_3)_3$), −1.2 ($^1J_{Si,C} = 45.1$ Hz, $SiMe_2$). ^{19}F NMR (C_6D_6, 298 K): δ −125.6 (br s, 2 F, *o*-F), −144.6 (tt, $^3J_{F,F} = 20.9$ Hz, $^4J_{F,F} = 6.6$ Hz, 1 F, *p*-F), −161.4 (m, 2 F, *m*-F) [$\Delta\delta_{m,p} = 16.8$]. $^{29}Si\{^1H\}$ NMR (C_6D_6, 298 K): δ 15.9 ($SiMe_2$).

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Appendix A. Supplementary material

CCDC 783505 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (internat.) +44(1223)336-033, E-mail: deposit@ccdc.cam.ac.uk].

Appendix. Supplementary material

Supplementary data related to this article can be found online at doi:10.1016/j.jorganchem.2010.09.024.

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