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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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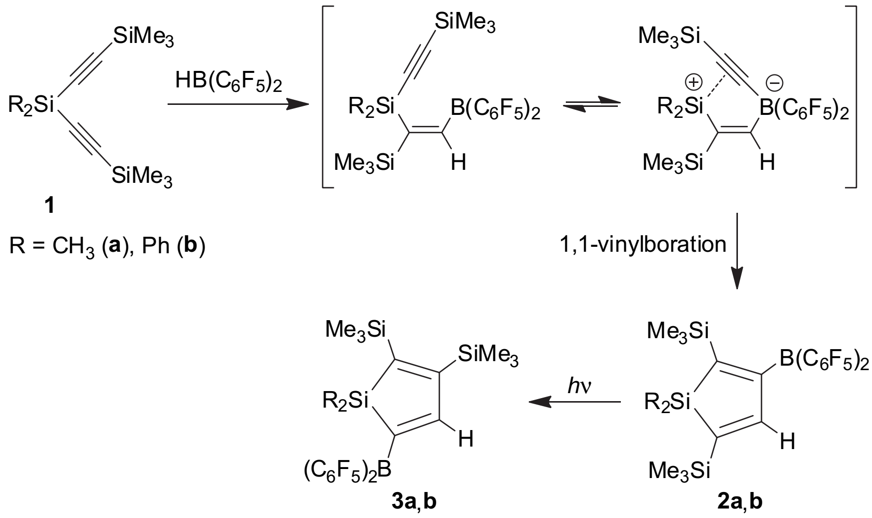


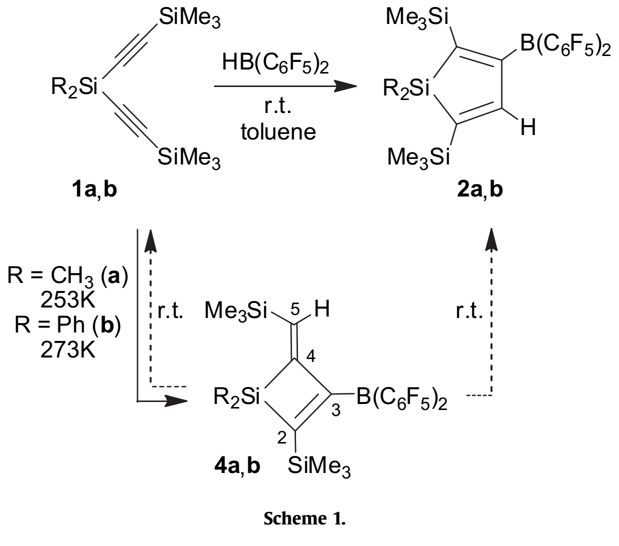
Chart 1.

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

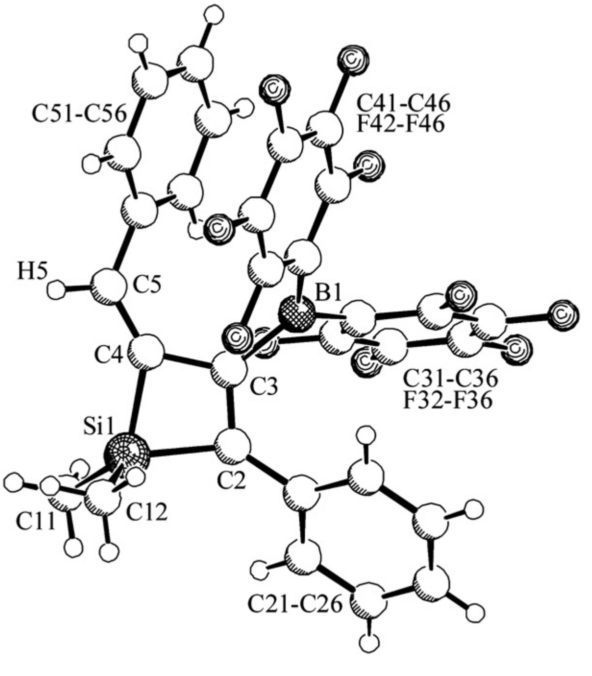


Fig. 1. Molecular structure of compound *E*-**6**.