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# Photochemical isomerisation of boryl-substituted silole derivatives†‡

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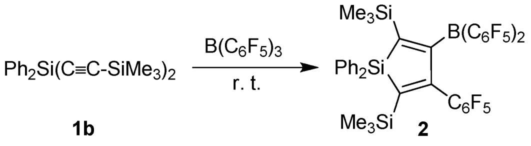
*Received (in Cambridge, UK) 23rd December 2009, Accepted 4th March 2010*
*First published as an Advance Article on the web 25th March 2010*
**DOI: 10.1039/b927221f**

**Bis(alkynyl)silanes (1a,b) react with bis(pentafluorophenyl)-borane to 3-boryl-2,5-bis(trimethylsilyl) substituted siloles 3a,b. Subsequent irradiation of 3 with Pyrex filtered UV light resulted in the complete conversion to the new 5-boryl-2,3-bis(trimethylsilyl) substituted siloles 4a,b.**

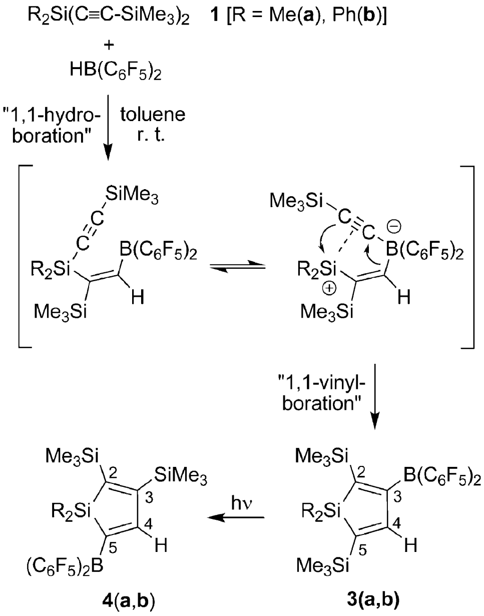
Siloles are increasingly important heterocycles. Suitably substituted or annelated derivatives are playing an increasingly significant role in materials chemistry.[1] Among these, boryl substituted derivatives are of special interest.[2] We had recently reported about the unconventional synthesis of the boryl silole system **2** that was prepared by means of treatment of the silyl acetylene derivative **1b** with the strong boron Lewis acid $B(C_6F_5)_3$ under ambient conditions (see Scheme 1).[2] This reaction involves a 1,1-carboboration reaction.[3] The resulting characteristic substitution pattern was secured by an X-ray crystal structure analysis. We now wish to report about an interesting new isomerisation reaction of such boryl functionalized siloles, bearing bulky silyl place holder groups at the α-positions, which proceeds rapidly upon photolysis. This reaction makes boryl substituted siloles with a different substitution pattern readily and cleanly available. This new silole rearrangement will here be described and discussed using a small series of novel boryl-silole derivatives that we have prepared by treatment of the parent silyl acetylenes (**1**) with "Piers' borane" $[HB(C_6F_5)_2]$.[4]



Scheme 1

We treated bis(trimethylsilylethynyl)dimethylsilane (**1a**) with one molar equivalent of $HB(C_6F_5)_2$ in toluene solution at room temperature. Workup after one day gave the product (**3a**) as a viscous oil (isolated in > 70% yield). Due to the consistency of the product we were not able to get it completely solvent free and analytically pure, but its identification as the β-boryl substituted silole derivative followed from its characteristic spectroscopic features and a comparison with **2** (see above). Compound **3a** shows $^{13}C$ NMR signals of the C4 framework at $\delta$ 174.2 (br, C3), 159.8 (C2), 150.9 (C4) and 149.9 (C5). The C(4)–H $^1H$ NMR signal was located at $\delta$ 7.42 ($^3J_{Si,H}$ = 16.9 Hz, $^3J_{Si,H}$ = 7.5 Hz). The compound features a pair of $^{29}Si$ NMR resonances of the $SiMe_3$ substituents at $\delta$ −7.1 and −9.6 (with corresponding $^1H$ NMR signals at $\delta$ 0.16 and −0.02) in addition to the $Me_2Si$ $^{29}Si$ NMR feature at $\delta$ 25.6. The broad $^{11}B$ NMR resonance indicates the presence of a tricoordinate boron center ($\delta$ 64) which is supported by the typical large m/p separation of the $C_6F_5$ $^{19}F$ NMR signals of compound **3a** [$\delta$ −126.4 (o), −143.6 (p), −160.7 (m)].[5] The reaction of the bis(trimethylsilylethynyl)diphenylsilane starting material (**1b**) with $HB(C_6F_5)_2$ proceeded analogously and gave the silole derivative **3b** as a yellow oil in > 70% yield. For both compounds we assume a reaction pathway involving a sequence of a formal 1,1-hydroboration followed by a 1,1-alkenylboration reaction (see Scheme 2).[6]

The 1,1-dimethyl-2,5-bis(trimethylsilyl)-3-borylsilole **3a** rearranged cleanly to the corresponding 2,3-bis(trimethylsilyl)-5-boryl isomer (**4a**) upon photolysis. Irradiation of compound **3a** with Pyrex filtered UV light (HPK 125) in toluene solution at room temperature for 4 h resulted in a practically complete conversion to **4a** that was isolated as a solid in close to 80% yield. The new compound was characterized by C,H-elemental analysis, spectroscopically and by X-ray diffraction



Scheme 2

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† Dedicated to Professor Karl-Heinz Thiele on the occasion of his 80th birthday.

‡ Electronic supplementary information (ESI) available: Text and figures giving further experimental and spectroscopic details. CCDC 765606 (**1a**) and 765607 (**4a**). For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/b927221f

§ X-Ray structure analysis.

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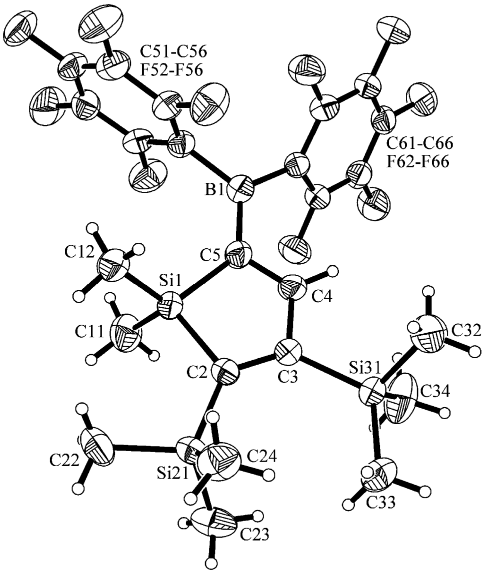
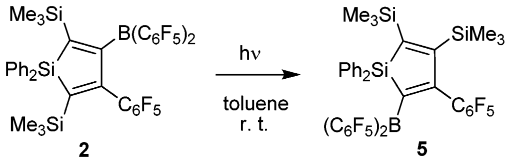


**Fig. 1** Molecular structure of the photoproduct **4a** (50% probability of thermal ellipsoids).

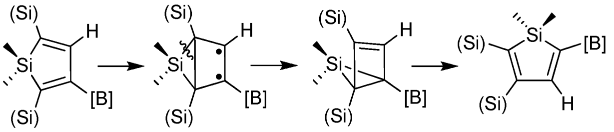
(single crystals were obtained from pentane at −30 °C).[7] In the crystal compound **4a** features a planar five-membered heterocyclic framework [Si1–C2: 1.892(3) Å, Si1–C5: 1.866(3) Å, angle C2–Si1–C5: 93.5(2)°] with an alternating C4-unit [C2–C3: 1.368(4) Å, C3–C4: 1.494(4) Å, C4–C5: 1.357(5) Å]. Carbon atoms C2 and C3 carry the bulky trimethylsilyl substituents [C2–Si21: 1.876(3) Å, angle Si21–C2–C3: 130.9(3)°, C3–Si31: 1.899(3) Å, angle Si31–C3–C2: 133.7(3)°] and the $-B(C_6F_5)_2$ substituent is attached at the α-carbon atom C5 [C5–B1: 1.523(5) Å]. The boron atom in compound **4a** is planar tricoordinate (sum of the bonding angles: 360.0°) (Fig. 1). Compound **4a** shows a $^{11}$B NMR resonance at $\delta$ 61 and $^{29}$Si NMR signals at $\delta$ 24.3 ($SiMe_2$) and $\delta$ −7.2 and −10.1 ($SiMe_3$). The $^{13}$C NMR resonances of the central carbon framework occur at $\delta$ 181.1 ($^1J_{Si,C}$ = 58.3 Hz, $^1J_{Si,C}$ = 42.2 Hz, C2), 172.1 (C4, $^1$H NMR: $\delta$ 8.11, $^3J_{Si,H}$ = 14.3 Hz), 171.5 ($^1J_{Si,C}$ = 61.7 Hz, C3) and 151.6 (br, C5).

Photolysis of the $Ph_2Si$-containing compound **3b** proceeded analogously. After 2 h irradiation time workup gave the rearranged product **4b** in *ca.* 71% yield (Scheme 2, for details see the ESI‡). We have also photolyzed the previously reported $C_6F_5$ substituted analogue **2** (see Scheme 1). The photolysis reaction required 6 h irradiation time to go to completion and we isolated the isomer **5** in 58% yield from the workup procedure (see Scheme 3).

These photolytic isomerisation reactions formally proceed by mutual exchange of the C3-[B] and C5-[Si] moieties at the five-membered heterocyclic framework. Although the mechanistic details of this reaction still have to be elucidated, this framework reorganization formally corresponds to the pattern of the di-π-methane rearrangement.[8,9] Scheme 4 shows a schematic representation of the necessary bond breaking and forming processes without implying that the depicted formulae represent actual intermediates involved in these rearrangements.



**Scheme 3**



**Scheme 4**

This study shows that the boryl-functionalized siloles of the types **2** and **3**, bearing the conjugated boryl substituent in the β-position, which are readily available from corresponding sila-acetylene and borane precursors by the unique 1,1-hydro-(or -carbo-)boration/1,1-vinylboration sequence, rearrange readily and completely to their α-boryl regioisomers upon photolysis. This combination of easily performed reactions will probably make a variety of siloles with useful substituent patterns readily available for applications in *e.g.* materials science and elsewhere.

Financial support from the Fonds der Chemischen Industrie and the Deutsche Forschungsgemeinschaft is gratefully acknowledged. We thank the BASF for a gift of solvents.

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7 **4a**: the bright yellow solution of bis(trimethylsilylethynyl)dimethylsilane (**1a**) (365 mg, 1.445 mmol) and bis(pentafluorophenyl)borane (500 mg, 1.445 mmol) in toluene (50 mL) was stirred overnight. Subsequently the solution was irradiated for 4 hours to finally get **4a** as a yellow-brown solid (79%, 685 mg). Crystals suitable for X-ray diffraction were obtained from a concentrated pentane solution at −30 °C. $C_{24}H_{25}BF_{10}Si_3$ (598.5): calcd. C 48.16, H 4.21;

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found C 47.69, H 4.25. Crystal data for $C_{24}H_{25}BF_{10}Si_3$ (**4a**), $M$ = 598.52, monoclinic, space group $C2/c$ (No. 15), $a$ = 26.7841(7), $b$ = 6.5724(2), $c$ = 33.4388(9) Å, $\beta$ = 107.519(1)°, $V$ = 5613.4(3) Å$^3$, $D_c$ = 1.416 g cm$^{-3}$, $\mu$ = 0.248 mm$^{-1}$, $Z$ = 8, $\lambda$ = 0.71073 Å, $T$ = 223(2) K, 21 439 reflections collected ($\pm h$, $\pm k$, $\pm l$), [(sin$\theta$)/$\lambda$] = 0.66 Å$^{-1}$, 6379 independent ($R_{int}$ = 0.071), and 4407 observed reflections [$I \geq 2\sigma(I)$], 351 refined parameters, $R$ = 0.068, w$R_2$ = 0.157. CCDC 765607 [for details see the ESI‡].

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