Unusual Product Formation in a 1,1-Carbaboration Reaction

Supporting Information

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General Information. All syntheses involving air- and moisture-sensitive compounds were carried out using standard Schlenk-type glassware (or in a glove box) under an atmosphere of argon. Solvents were dried and stored under an argon atmosphere. The following instruments were used for physical characterization of the compounds: Bruker AMX400 (1H: 400 MHz, 13C: 101 MHz), Varian UnityPlus 600 (1H: 600 MHz, 13C: 151 MHz, 19F: 564 MHz, 11B: 192 MHz, 31P: 243 MHz). 1H NMR and 13C NMR: chemical shift δ is given relative to TMS and referenced to the solvent signal. 19F NMR: chemical shift δ is given relative to CFCl$_3$ (δ(CFCl$_3$) = 0, external reference); 11B NMR: chemical shift δ is given relative to BF$_3$·Et$_2$O (δ(BF$_3$·Et$_2$O) = 0, external reference). NMR assignments are supported by additional 2D NMR experiments. Elemental analyses were performed on a Elementar Vario El III. IR spectra were recorded on a Varian 2100 FT-IR (Excalibur Series). Melting points were obtained with a DSC Q20 (TA Instruments).

X-Ray diffraction: Data sets were collected with a Bruker APEX CCD diffractometer. Programs used: data collection: APEX2 V2014.5-0 (Bruker AXS Inc., 2014); cell refinement: SAINT V8.34A (Bruker AXS Inc., 2013); data reduction: SAINT V8.34A (Bruker AXS Inc., 2013); absorption correction, SADABS V2014/2 (Bruker AXS Inc., 2014); structure solution SHELXT-2014 (Sheldrick, 2014); structure refinement SHELXL-2014 (Sheldrick, 2014) and graphics, XP (Bruker AXS Inc., 2014). Thermals ellipsoids are shown with 50% probability. R-values are given for observed reflections, and wR$^2$ values are given for all reflections. [ a) Bruker (2013). APEX2, SAINT and SADABS Bruker AXS Inc., Madison, Wisconsin, USA. b). SHELXT and SHELXL Sheldrick, G. M. Acta Cryst., 2008, A64, 112–122.] The CCDC number is 1044793.
Syntheses of alkynes

The alkynes I and 1 were synthesized by using a slight modification of a procedure described in the literature: R. Emanuelsson, A. Wallner, E. A. M. Ng, J. R. Smith, D. Nauroozi, S. Ott, H. Ottosson, Angew. Chem., Int. Ed., 2013, 52, 983.

Synthesis of 4-Methyl-1-(trimethylsilyl)-3-[2-(trimethylsilyl)ethynyl]pent-1-yn-3-ol (I)

\[
\text{Me}_3\text{Si} \equiv \text{H} + n-\text{BuLi} \rightarrow \text{HO} \text{Me}_3\text{Si} \equiv \text{SiMe}_3
\]

Trimethylsilylacetylene (4.10 mL, 2.83 g, 28.8 mmol, 2.0 eq.) was dissolved in thf (30 mL) and cooled to -78 °C. n-BuLi (1.6 M in hexane, 19.8 mL, 31.7 mmol, 1.1 eq.) was added and the obtained reaction mixture was stirred for 20 min at -78 °C. Thereafter methyl isobutyrate (1.65 mL, 1.47 mg, 14.4 mmol, 1.0 eq.) was added. Then the cooling bath was removed. After reaching room temperature the reaction mixture was quenched with sat. aqueous NH₄Cl (10 mL). The layers were separated and the aqueous layer was washed with Et₂O (2 x 30 mL). The combined organic phases was washed with brine (20 mL), dried over MgSO₄ and filtrated. Then all volatiles were removed in vacuo to give compound I (3.82 g, 14.4 mmol, 100%) as a colorless oil.

\(^1\text{H NMR}\) (400 MHz, 296 K, CD₂Cl₂): \(\delta = 2.52\) (s, 1H, OH), \(1.96\) (sept, \(3J_{HH} = 6.7\) Hz, 1H, CH), \(1.06\) (d, \(3J_{HH} = 6.7\) Hz, 6H, CH₃), \(0.19\) (s, \(2J_{SiH} = 7.1\) Hz, 18H, SiCH₃).

\(^{13}\text{C}{^1}\text{H} \text{NMR}\) (101 MHz, 296 K, CD₂Cl₂): \(\delta = 104.8\) (C≡), 88.9 (≡CSi), 68.6 (COH), 40.2 (CH), 17.4 (CH₃), −0.3 (\(3J_{SiC} = 56.3\) Hz, SiCH₃).

\(^{29}\text{Si}{^1}\text{H} \text{ DEPT}\) (119 MHz, 299 K, CD₂Cl₂): \(\delta = -17.1\) (\(\nu_{1/2} \sim 1\) Hz).


Synthesis of 1-Trimethylsilyl-3-trimethylsilylethynyl-4-methylpent-3-en-1-yne (1)

A solution of compound I (2.0 g, 7.5 mmol, 1.0 eq) and p-toluenesulfonic acid (50 mg, 0.29 mmol, 0.04 eq.) in toluene (150 mL) was refluxed for 3 h with a Dean-Stark trap. Thereafter p-toluenesulfonic acid (60 mg, 0.35 mmol, 0.05 eq.) was added and the reaction mixture was refluxed for further 12 h. The resulting reaction mixture was washed with H₂O (2 x 30 mL) and with sat.
aqueous NaCl (30 mL). Then the organic phase was dried with MgSO4, filtrated and all volatiles of the filtrate were removed *in vacuo*. The obtained residue was purified by column chromatography (silica / n-pentane) to give the compound 1 (0.823 g, 3.3 mmol, 44%) as a colorless oil.

**¹H NMR** (400 MHz, 296 K, CD₂Cl₂): δ = 2.01 (s, 1H, CH₃), 0.20 (s, 2J_SiH = 7.2 Hz, 3H, SiCH₃)

**¹³C{¹H} NMR** (101 MHz, 296 K, CD₂Cl₂): δ = 158.1, 101.7, 101.6 (C=C, C≡), 96.7 (≡CSi), 22.8 (CH₃), 0.0 (1J_SiC = 55.8 Hz, SiCH₃).

**²⁹Si{¹H} DEPT** (119 MHz, 299 K, CD₂Cl₂): δ = −17.8 (ν₁/₂ ~ 1 Hz).


### Generation of compound 4 (NMR scale)

![Diagram of compound 1 and 4](image)

A solution of B(C₆F₅)₃ (20.6 mg, 0.04 mmol, 1.0 eq.) in dichloromethane-d₂ (0.5 mL) was added to a solution of compound 1 (10.0 mg, 0.04 mmol, 1.0 eq.) in dichloromethane-d₂ (0.5 mL). After 1 h at room temperature the reaction mixture was characterized by NMR experiments:

- **4** (major isomer) : **4** (minor isomer) : **1** ~ 82 : 12 : 6
- Major isomer (tentatively assigned as E-isomer):
  - **¹H NMR** (600 MHz, 299 K, CD₂Cl₂): δ = 1.80 (m, 1H, CH₃[Z]), 1.69 (s, 1H, CH₃[E]), 0.15 (s, 2J_SiH = 7.0 Hz, 3H, SiCH₃), 0.10 (s, 2J_SiH = 7.0 Hz, 3H, ≡SiCH₃).
  - **¹³C{¹H} NMR** (151 MHz, 299 K, CD₂Cl₂): δ = 170.7 (1J_SiC = 59.0 Hz, ≡CSi), 142.9, 119.7 (C=C), 142.7 (br, =CB), 102.6 (1J_SiC = 15.5 Hz, C≡), 99.2 (1J_SiC = 85.2 Hz, ≡CSi), 23.0 (CH₃[Z]), 21.7 (m, CH₃[E]), 1.4 (1J_SiC = 53.3 Hz, ≡SiCH₃), −0.2 (1J_SiC = 56.1 Hz, SiCH₃), [C₆F₅ not listed].
  - **¹H, ¹³C GHQC** (600 MHz / 151 MHz, 299 K, CD₂Cl₂): δ ¹H / δ ¹³C = 1.80 / 23.0 (CH₃[Z]), 1.69 / 21.7 (CH₃[E]), 0.15 / −0.2 (SiCH₃), 0.10 / 1.4 (≡SiCH₃).
  - **¹H, ¹³C GHMBC** (600 MHz / 151 MHz, 299 K, CD₂Cl₂): [selected traces]: δ ¹H / δ ¹³C = 1.80 / 142.9, 119.7, 102.6, 21.7 (CH₃[Z] / C=C, C≡, CH₃[E]), 0.15 / 99.2, −0.2 (SiCH₃ / ≡CSi, SiCH₃), 0.10 / 170.7, 1.4 (≡SiCH₃ / ≡CSi, ≡SiCH₃).
  - **¹¹B{¹H} NMR** (192 MHz, 299 K, CD₂Cl₂): δ = 62.7 (ν₁/₂ ~ 1600 Hz).

- **¹⁹F NMR** (564 MHz, 299 K, CD₂Cl₂): δ = −126.7 (m, 2F, o), −146.2 (tt, 3J_FF = 20.2 Hz, 4J_FF = 5.1 Hz, 1F, p), −161.4 (m, 2F, m)(BC₆F₅)[Δδ¹⁹F_m,pB = 15.2], −132.4, −138.2 (each br, 1F, o), −155.7 (t, 3J_FF = 20.4 Hz, 1F, p), −162.7, −163.7 (each br, 1F, m)(C₆F₅)[Δδ¹⁹F_m,p = 7.0, 8.0].
$^{29}$Si/$^1$H DEPT (119 MHz, 299 K, CD$_2$Cl$_2$): $\delta = -1.7 (^{1}\text{SiCH}_3, \nu_{1/2} \sim 2 \text{ Hz}), -18.2 (\text{SiCH}_3, \nu_{1/2} \sim 2 \text{ Hz})$.

$^1$H, $^{29}$Si GHMQC (600 MHz / 119 MHz, 299 K, CD$_2$Cl$_2$): $\delta ^{29}$Si / $\delta ^1$H= −1.7 / 1.80, 1.69, 0.10 ($^{1}$SiCH$_3$ / CH$_3^Z$, CH$_3^E$, $^{29}$SiCH$_3$), −18.2 / 1.80, 1.69, 0.15 (SiCH$_3$ / CH$_3^Z$, CH$_3^E$, $^{29}$SiCH$_3$).

$^1$H, $^{19}$F GHOESY (600 MHz / 564 MHz, 299 K, CD$_2$Cl$_2$)[selected traces]: $\delta ^1$H / $\delta ^{19}$F = 0.10 / −126.7, −161.4 ($^{1}$SiCH$_3$ / $\alpha$-BC$_6$F$_5$, $m$-BC$_6$F$_5$).

Minor isomer (tentatively assigned as Z-isomer) (selected NMR data):

$^1$H NMR (600 MHz, 299 K, CD$_2$Cl$_2$): $\delta = 1.79 (m, 1H, CH$_3^Z$), 1.67 (s, 1H, CH$_3^E$), 0.24 (s, $^2J_{\text{SiH}} = 6.9 \text{ Hz}$, 3H, $^{29}$SiCH$_3$), 0.20 (s, $^2J_{\text{SiH}} = 6.9 \text{ Hz}$, 3H, SiCH$_3$).

$^{13}$C/$^1$H NMR (151 MHz, 299 K, CD$_2$Cl$_2$): $\delta = 168.0 (=\text{CSi}), 142.4, 119.2 (\text{C=C}), 102.7 (\text{C=}), 96.7 (=\text{CSi}), 22.7 (\text{CH$_3^Z$}), 21.5 (m, \text{CH$_3^E$}), 1.0 (^{1}\text{SiCH}_3), 0.0 (\text{SiCH}_3), [\text{n.o.} =\text{CB, C$_6$F$_5$} \text{ not listed}]$.

$^1$H, $^{13}$C GHSQC (600 MHz / 151 MHz, 299 K, CD$_2$Cl$_2$): $\delta ^1$H / $\delta ^{13}$C = 1.79 / 22.7 (CH$_3^Z$), 1.67 / 21.5 (CH$_3^E$), 0.24 / 1.0 ($^{1}$SiCH$_3$), 0.20 / 0.0 (SiCH$_3$).

$^1$H, $^{13}$C GHMBC (600 MHz / 151 MHz, 299 K, CD$_2$Cl$_2$)[selected traces]: $\delta ^1$H / $\delta ^{13}$C = 0.24 / 168.0, 1.0 ($^{1}$SiCH$_3$ / $=\text{CSi}$, $^{29}$SiCH$_3$), 0.20 / 96.7 (SiCH$_3$ / $=\text{CSi}$).

$^{29}$Si/$^1$H DEPT (119 MHz, 299 K, CD$_2$Cl$_2$): $\delta = -1.3 (^{1}\text{SiCH}_3, \nu_{1/2} \sim 2 \text{ Hz}), -17.8 (\text{SiCH}_3, \nu_{1/2} \sim 1 \text{ Hz})$.

$^1$H, $^{29}$Si GHMQC (600 MHz / 119 MHz, 299 K, CD$_2$Cl$_2$): $\delta ^{29}$Si / $\delta ^1$H= −1.3 / 0.24 ($^{1}$SiCH$_3$ / $^{29}$SiCH$_3$), −17.8 / 0.20 (SiCH$_3$ / $^{29}$SiCH$_3$).

$^1$H NMR (600 MHz, 299 K, CD$_2$Cl$_2$ (*) spectrum of 4.

$^1$H NMR (600 MHz, 299 K, CD$_2$Cl$_2$ (*) spectrum of 4.
$^{13}\text{C}[^1\text{H}]$ NMR (151 MHz, 299 K, CD$_2$Cl$_2$) spectrum of 4.

$^{19}\text{F}$ NMR (564 MHz, 299 K, CD$_2$Cl$_2$) spectrum of 4.

$^{11}\text{B}[^1\text{H}]$ NMR (192 MHz, 299 K, CD$_2$Cl$_2$), and $^{29}\text{Si}[^1\text{H}]$ DEPT (119 MHz, 299 K, CD$_2$Cl$_2$) spectra of 4.
A solution of tris(pentafluorophenyl)borane (50.0 mg, 0.20 mmol, 1.0 eq.) in toluene (3 mL) was added to a solution of compound 1 (103.0 mg, 0.20 mmol, 1.0 eq.) in toluene (2 mL). The yellow reaction mixture was stirred for 1 h at room temperature. Thereafter the reaction mixture was heated to 60 °C for 4.5 h. Subsequently all volatiles were removed *in vacuo* and *n*-pentane was added. The resulting yellow suspension was stirred for 1 h, whereupon the supernatant solution was removed *via* syringe. The residue was dried *in vacuo* to give the compound 3 (62.0 mg, 0.082 mmol, 41%) as a yellow powder. Crystals of compound 3 suitable for the single crystal structure analysis were obtained from a *n*-pentane solution of compound 3 at −32 °C.

**Elemental Analysis** calcd for C_{32}H_{24}BF_{15}Si_{2}: C 50.54, H 3.18; found C 50.54, H 3.00.

**IR** (KBr) \( \nu \ [\text{cm}^{-1}] = 2958 \ (w), 2875 \ (w), 1649 \ (w), 1519 \ (s), 1493 \ (s), 1418 \ (s), 1389 \ (w), 1311 \ (m), 1251 \ (m), 1131 \ (m), 1077 \ (m), 983 \ (s), 842 \ (s), 757 \ (w), 685 \ (w), 625 \ (w), 551 \ (w), 503 \ (w), 468 \ (w). \)

**\(^1\)H NMR** (600 MHz, 299 K, CD\(_2\)Cl\(_2\)): \( \delta = 3.34 \ (m, 1H, H1), 2.89 \ (m, 1H, H8), 2.75, 1.47 \ (dd, \ J_{HH} = 19.0 \ Hz, \ J_{HH} = 10.8 \ Hz) \) (each 1H, H2), 2.73, 1.78 \ (ddd \ J_{HH} = 13.4 \ Hz, \ J_{HH} = 4.1 \ Hz, \ J_{HH} = 0.7 \ Hz) \) (each 1H, H9), −0.19 \ (s, \ J_{SiH} = 6.7 \ Hz, 9H, 8-SiCH\(_3\)), −0.32 \ (s, \ J_{SiH} = 6.6 \ Hz, 9H, 5-SiCH\(_3\)).

**\(^{13}\)C{\(^1\)H} NMR** (151 MHz, 299 K, CD\(_2\)Cl\(_2\)): \( \delta = 179.8 \ (C5), 150.4 \ (d, \ J_{FC} = 0.9 \ Hz, C6), 144.6 \ (br, C4), 126.5 \ (m, C7), 47.0 \ (C1), 39.2 \ (d, \ J_{FC} = 1.9 \ Hz, C8), 38.6 \ (br, C2), 32.8 \ (C9), −0.2 \ (d, \ J_{FC} = 1.4 \ Hz, \ J_{SiC} = 53.4 \ Hz, 5-SiCH\(_3\)), −2.6 \ (\ J_{SiC} = 51.1 \ Hz, 8-SiCH\(_3\)), \) [C\(_6\)F\(_5\) not listed].

**\(^{13}\)C{\(^1\)H,\(^{19}\)F} NMR** (151 MHz, 299 K, CD\(_2\)Cl\(_2\)) [selected resonances]: \( \delta = 150.4 \ (C6), 146.1 \ (o), 142.3 \ (p), 137.5 \ (m), 114.2 \ (br, \ \ J(BC6F5)), 145.3 \ (o'), 145.0 \ (o), 141.4 \ (p), 138.6 \ (m), 138.09 \ (m'), 113.8 \ (i)(C6F\(_5\)), 144.6 \ (br, C4), 143.8 \ (o'), 143.6 \ (o), 140.5 \ (p), 138.14 \ (m'), 137.4 \ (m), 118.4 \ (i) (C6F\(_5\)), 126.5 \ (C7), 39.2 \ (C8), \) [tentatively assigned].

**\(^1\)H, \(^1\)H GOCOSY** (600 MHz / 600 MHz, 299 K, CD\(_2\)Cl\(_2\)) [selected traces]: \( \delta ^1H / \delta ^1H = 3.34 / 2.75, 1.78, 1.47 \) (H1 / H2, H9, H2), 2.89 / 2.73, 1.78 (H8 / H9, H9).

**\(^1\)H, \(^{13}\)C GHSSQC** (600 MHz / 151 MHz, 299 K, CD\(_2\)Cl\(_2\)): \( \delta ^1H / \delta ^{13}C = 3.34 / 47.0 \) (H1 / C1), 2.89 / 39.2 (H8 / C8), 2.75 / 38.6 (H2 / C2), 2.73 / 32.8 (H9 / C9), 1.78 / 32.8 (H9 / C9), 1.47 / 38.6 (H2 / C2), −0.19 / −2.6 (8-SiCH\(_3\)), −0.32 / −0.2 (5-SiCH\(_3\)).

**\(^1\)H, \(^{13}\)C GHMBC** (600 MHz / 151 MHz, 299 K, CD\(_2\)Cl\(_2\)) [selected traces]: \( \delta ^1H / \delta ^{13}C = 3.34 / 150.4, 126.5 \) (H1 / C6, C7), 2.89 / 179.8, 150.4, 126.5, 38.6, 32.8, −2.6 (H8 / C5, C6, C7, C2, C9), 2.74 / 150.4, 144.6 (H2 / C6, C4), −0.19 / 39.2, −2.6 (8-SiCH\(_3\) / C8, 8-SiCH\(_3\)), −0.32 / 179.8, −0.2 (5-SiCH\(_3\) / C5, 5-SiCH\(_3\)).

**\(^{11}\)B{\(^1\)H} NMR** (192 MHz, 299 K, CD\(_2\)Cl\(_2\)): \( \delta = 67.3 \ (\nu_{1/2} \sim 1200 \ Hz). \)
$^{19}\text{F NMR}$ (564 MHz, 299 K, CD$_2$Cl$_2$): $\delta = -132.3$ (m, 2F, o), $-152.0$ (t, $^{3}J_{FF} = 19.8$ Hz, 1F, p), $-162.0$ (m, 2F, m)(BC$_6$F$_5$)$[\Delta\delta^{19}\text{F}_{m,pB} = 10.0]$, $-135.4$ (m, o), $-136.9$ (m, o'), $-154.7$ (t, $^{3}J_{FF} = 20.9$ Hz, p), $-162.1$ (m, m), $-163.2$ (m, m')(each 1F, C$_6$F$_5$)$[\Delta\delta^{19}\text{F}_{m,p4} = 8.4, 8.5]$, $-139.6$ (m, o), $-140.0$ (m, o'), $-156.2$ (t, $^{3}J_{FF} = 21.3$ Hz, p), $-162.4$ (m, m'), $-163.4$ (m, m)(each 1F, C$_6$F$_5$)$[\Delta\delta^{19}\text{F}_{m,p1} = 6.2, 7.2]$. $^{19}\text{F},^{19}\text{F GCOSY}$ (564 MHz / 564 MHz, 299 K, CD$_2$Cl$_2$)[selected traces]: $\delta^{19}\text{F} / \delta^{19}\text{F} = -162.0 / -132.3$, $-152.0$ (m / o, p)(BC$_6$F$_5$), $-162.1 / -135.4, -136.9, -154.7$ (m / o, o, p), $-163.2 / -135.4, -136.9, -154.7$ (m / o, o, p)(C$_6$F$_5$)$_4$, $-162.4 / -139.6, -156.2$ (m / o, p), $-163.4 / -139.6, -156.2$ (m / o, p)(C$_6$F$_5$)$_4$. $^{1}\text{H},^{19}\text{F GHOESY}$ (600 MHz / 564 MHz, 299 K, CD$_2$Cl$_2$) [selected traces]: $\delta^{1}\text{H} / \delta^{19}\text{F} = 2.89 / -136.9$ (H5 / o-C$_6$F$_5$)$_4$, 2.74 / -132.3 (H8 / o-BC$_6$F$_5$).

$^{29}\text{Si}{^{1}}\text{H} \text{ DEPT}$ (119 MHz, 299 K, CD$_2$Cl$_2$): $\delta = 2.2$ ($\nu_{1/2} = 2$ Hz)(8-SiCH$_3$), $-3.1$ ($\nu_{1/2} = 2$ Hz)(5-SiCH$_3$) $^{29}\text{Si},^{1}\text{H GHMDC}$ (119 MHz / 600 MHz, 299 K, CD$_2$Cl$_2$): $\delta^{29}\text{Si} / ^{1}\text{H} = 2.2 / 3.34, 2.89, 2.75, 2.73, 1.78, -0.19$ (8-SiCH$_3$ / H1, H8, H2, H9, 8-SiCH$_3$), $-3.1 / -0.32$ (5-SiCH$_3$ / 5-SiCH$_3$).

$^{1}\text{H}$

$^{13}\text{C}{^{1}}\text{H}$

$^{13}\text{C}{^{1}}\text{H} \text{ NMR}$ (151 MHz, 299 K, CD$_2$Cl$_2$(*)) spectrum of 3.

$^{1}\text{H NMR}$ (600 MHz, 299 K, CD$_2$Cl$_2$(*)) spectrum of 3.
Top: $^{13}$C($^1$H) NMR (151 MHz, 299 K, CD$_2$Cl$_2$) spectrum of 3; bottom: $^{13}$C($^1$H, $^{19}$F) NMR (151 MHz, 299 K, CD$_2$Cl$_2$) spectrum of 3.

$^{19}$F/$^{13}$C GHSQC (564 / 151 MHz, 299 K, CD$_2$Cl$_2$) spectrum of 3.
$^{19}$F NMR (564 MHz, 299 K, CD$_2$Cl$_2$) spectrum of 3.

$^{11}$B{$^1$H} NMR (192 MHz, 299 K, CD$_2$Cl$_2$) and $^{29}$Si{$^1$H} DEPT (119 MHz, 299 K, CD$_2$Cl$_2$) spectra of 3.
X-ray crystal structure analysis of compound 3, formula C_{32}H_{24}BF_{15}Si_{2}, M = 760.50, yellow crystal, 0.200 x 0.200 x 0.080 mm, a = 13.878(3), b = 14.2041(3), c = 19.8693(3) Å, α = 101.859(1), β = 98.658(1), γ = 117.694(1)°, V = 3254.5(1) Å³, ρ_{calc} = 1.552 g cm⁻³, μ = 2.009 mm⁻¹, empirical absorption correction (0.608 ≤ T ≤ 0.753), Z = 4, triclinic, space group P 1 (No. 2), λ = 1.54178 Å, T = 100(2) K, ω and φ scans, 44786 reflections collected, 11780 independent (R_{int} = 0.075) and 9044 observed reflections [I > 2σ(I)], 913 refined parameters, R = 0.045, wR² = 0.116, max. (min.) residual electron density 0.41 (-0.31) e Å⁻³, hydrogen atoms were calculated and refined as riding atoms.

Control experiment:

(A) A solution of tris(pentafluorophenyl)borane (41.2 mg, 0.08 mmol, 2.0 eq.) in dichloromethane-d₂ (1 mL) was added to a solution of compound 1 (10.0 mg, 0.04 mmol, 1.0 eq.) in dichloromethane-d₂ (1 mL). The yellow reaction mixture was stirred for 30 h at room temperature and then stored at −20 °C for 24 h. Thereafter the reaction mixture was analyzed by NMR experiments. The NMR spectra showed the formation of mainly the E-isomer of compound 4.

top: ¹H NMR (600 MHz, 299 K, CD₂Cl₂ (*)) spectrum of compound 4 (see above); bottom: ¹H NMR (600 MHz, 299 K, CD₂Cl₂ (*)) spectrum of the reaction mixture of compound 1 + 2 B(C₆F₅)₃.
Then the reaction mixture was stored for further 4 d at room temperature and then heated to 40 °C for 7 h. The obtained NMR spectra showed a mixture of the E-Isomer of compound 4 : Z-Isomer of compound 4 : unidentified product : compound 3 in a ratio of ca. 9 : 1 : 5.5 : 9 (1H).
A: $^1$H NMR (600 MHz, 299 K, CD$_2$Cl$_2$) spectrum of compound 4 (see above); B: $^1$H NMR (600 MHz, 299 K, CD$_2$Cl$_2$) spectrum of the reaction mixture of compound 1 + 2 B(C$_6$F$_5$)$_3$; C: $^1$H NMR (600 MHz, 299 K, CD$_2$Cl$_2$) spectrum of the reaction mixture of compound 1 + 2 B(C$_6$F$_5$)$_3$ [4d r.t., 7 h 40 °C]; D: $^1$H NMR (600 MHz, 299 K, CD$_2$Cl$_2$) spectrum of compound 3 (see above); #: unidentified product.
(C) Subsequently the reaction mixture was heated for further 7.5 h at 45 °C. The NMR spectra showed a mixture of compound 3 (as the main compound ca. 80%) : B(C₆F₅)₃ (1 :1) and unidentified products (20%) (determined by ¹H NMR and ¹⁹F NMR).
A: $^1$H NMR (600 MHz, 299 K, CD$_2$Cl$_2$ (*)) spectrum of compound 4 (see above); B: $^1$H NMR (600 MHz, 299 K, CD$_2$Cl$_2$ (*)) spectrum of the reaction mixture 1 + 2 B(C$_6$F$_5$)$_3$; C: $^1$H NMR (600 MHz, 299 K, CD$_2$Cl$_2$ (*)) spectrum of the reaction mixture 1 + 2 B(C$_6$F$_5$)$_3$ 4 d r.t., 7 h 40 °C; D: $^1$H NMR (600 MHz, 299 K, CD$_2$Cl$_2$ (*)) spectrum of the reaction mixture 1 + 2 B(C$_6$F$_5$)$_3$ 4 d r.t., 7 h 40 °C, 7.5 h 45 °C; E: $^1$H NMR (600 MHz, 299 K, CD$_2$Cl$_2$ (*)) spectrum of compound 3 (see above); #: unidentified product.
A: $^1$H NMR (600 MHz, 299 K, CD$_2$Cl$_2$) spectrum of compound 4 (see above); B: $^1$H NMR (600 MHz, 299 K, CD$_2$Cl$_2$) spectrum of the reaction mixture 1 + 2 B(C$_6$F$_5$)$_3$; C: $^1$H NMR (600 MHz, 299 K, CD$_2$Cl$_2$) spectrum of the reaction mixture 1 + 2 B(C$_6$F$_5$)$_3$ 4d r.t., 7 h 40 °C; D: $^1$H NMR (600 MHz, 299 K, CD$_2$Cl$_2$) spectrum of the reaction mixture 1 + 2 B(C$_6$F$_5$)$_3$ 4d r.t., 7 h 40 °C, 7.5 h 45 °C; E: $^1$H NMR (600 MHz, 299 K, CD$_2$Cl$_2$) spectrum of compound 3 (see above); #: unidentified product.
A: $^{19}$F NMR (564 MHz, 299 K, CD$_2$Cl$_2$) spectrum of compound 4 (see above); B: $^{19}$F NMR (564 MHz, 299 K, CD$_2$Cl$_2$) spectrum of the reaction mixture $1 + 2 \text{B(C}_6\text{F}_5)_3$; C: $^{19}$F NMR (564 MHz, 299 K, CD$_2$Cl$_2$) spectrum of the reaction mixture $1 + 2 \text{B(C}_6\text{F}_5)_3$ 4d r.t., 7 h 40 °C; D: $^{19}$F NMR (564 MHz, 299 K, CD$_2$Cl$_2$) spectrum of the reaction mixture $1 + 2 \text{B(C}_6\text{F}_5)_3$ 4d r.t., 7 h 40 °C, 7.5 h 45 °C; E: $^{19}$F NMR (564 MHz, 299 K, CD$_2$Cl$_2$) spectrum of compound 3 (see above).

A: $^{29}$Si DEPT (119 MHz, 299 K, CD$_2$Cl$_2$) spectrum of compound 4 (see above); B: $^{29}$Si DEPT (119, 299 K, CD$_2$Cl$_2$) spectrum of the reaction mixture $1 + 2 \text{B(C}_6\text{F}_5)_3$; C: $^{29}$Si DEPT (119, 299 K, CD$_2$Cl$_2$) spectrum of the reaction mixture $1 + 2 \text{B(C}_6\text{F}_5)_3$ 4d r.t., 7 h 40 °C; D: $^{29}$Si DEPT (119, 299 K, CD$_2$Cl$_2$) spectrum of the reaction mixture $1 + 2 \text{B(C}_6\text{F}_5)_3$ 4d r.t., 7 h 40 °C, 7.5 h 45 °C; E: $^{29}$Si DEPT (119, 299 K, CD$_2$Cl$_2$) spectrum of compound 3 (see above).