Supporting Information for:

“Successive Carbene Insertion into 9-Phenyl-9-Borafluorene”

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Experimental details

**General Considerations:** All manipulations were performed under an inert atmosphere in a nitrogen-filled MBraun Unilab glove box or using standard Schlenk techniques. Benzene was purchased as ACS grade from Millipore Corporation, and C₆D₆ for NMR spectroscopy was purchased from Cambridge Isotope Laboratories. Both were dried by stirring for 3 days over CaH₂, distilled, and stored over 4 Å molecular sieves. All other solvents were purchased from commercial sources as anhydrous grade, dried further using a JC Meyer Solvent System with dual columns packed with solvent-appropriate drying agents, and stored over 4Å molecular sieves. 9-Phenyl-9-borafluorene (2Ph) was prepared by the literature procedure.¹ Trimethylsilyldiazomethane solution (2 M in hexanes) was purchased from Acros Organics and used as received. Multinuclear NMR spectra (¹H, ¹³C{¹H}, ¹¹B) were recorded on a Bruker Ascend 400 MHz instrument. High resolution mass spectra (HRMS) were obtained at the University of Texas at Austin Mass Spectrometry Center on a Micromass Autospec Ultima spectrometer using CI. Melting points were measured with a Thomas Hoover Uni-melt capillary melting point apparatus and are uncorrected. FT-IR spectra were recorded on a Bruker Alpha ATR FT-IR spectrometer on solid samples. Single crystal X-ray diffraction data were collected on a Bruker Apex II-CCD detector using Mo-Kα radiation (λ = 0.71073 Å). Crystals were selected under paratone oil, mounted on MiTeGen micromounts, and immediately placed in a cold stream of N₂. Structures were solved and refined using SHELXTL and figures produced using OLEX2.²

![Synthesis of 3](attachment:image.png)

**Synthesis of 3:** To a solution of 2Ph (28.0 mg, 0.117 mmol) in n-pentane (1 mL), trimethylsilyldiazomethane (2 M in hexanes, 0.067 mL, 0.134 mmol) was added dropwise at room temperature while stirring. The reaction mixture
was stirred for an additional 10 min, after which the volatiles were removed in vacuo. The product, a pale yellow solid, was determined to be pure by $^1$H NMR with no additional work-up. Single crystals for X-ray diffraction studies were grown from an n-pentane solution of 3 at -35 ºC. Yield: 38.0 mg (quantitative). d.p. 66-68 ºC.

$^1$H NMR (400 MHz, C$_6$D$_6$): $\delta$ 8.13 (dd, $J = 7.5$, 1.0 Hz, 1H), 8.07 (d, $J = 8.0$ Hz, 1H), 8.03-8.00 (m, 1H), 7.80 (dd, $J = 7.5$, 2.0 Hz, 2H), 7.46-7.42 (m, 1H), 7.35-7.29 (m, 3H), 7.26-7.12 (m, C$_6$D$_6$, 5H), 3.88 (s, 1H), -0.30 (s, 9H)

$^{13}$C${}^{(1)}$H NMR (101 MHz, C$_6$D$_6$): $\delta$ 144.65, 140.59, 136.01, 135.15, 134.42, 133.37, 130.14, 129.80, 127.20, 126.76, 125.61, 124.79, 123.98, 48.87, -0.20

$^{11}$B NMR (128 MHz, C$_6$D$_6$): $\delta$ 65.8

FT-IR (cm$^{-1}$ (ranked intensity)): 1593 (5), 1476 (12), 1439 (7), 1247 (2), 1038 (6), 952 (9), 826 (1), 766 (15), 746 (10), 730 (3), 702 (4), 659 (8), 544 (14), 486 (13), 439 (11)

High-resolution mass spectrometry (HRMS) chemical ionization (CI): calcd for C$_{22}$H$_{33}$BSi [M]$^+$, 326.1662; found, 326.1667.

Synthesis of 4: To a solution of 3 (83.0 mg, 0.254 mmol) in benzene (1.5 mL), trimethylsilyldiazomethane (2 M in hexanes, 0.128 mL, 0.256 mmol) was added dropwise at room temperature while stirring.
After 20 minutes of stirring, the volatiles were removed *in vacuo* to yield 4 as a white solid. The solid was then redissolved in a minimal amount of toluene, recrystallized at -35 °C, and dried *in vacuo*. Yield: 47.0 mg (45%). d.p. 66-68 °C.

Synthesis of 4 directly from 2Ph: To a solution of 2Ph (429.0 mg, 1.787 mmol) in benzene (5 mL), trimethylsilyldiazomethane (2 M in hexanes, 1.787 mL, 3.574 mmol) was added dropwise at room temperature while stirring. The reaction mixture was then heated for 1 d at 80 °C, after which the solvent was evaporated *in vacuo* to afford a pale yellow oil. Lyophilization of the crude oil from benzene (1 mL) provided a white powder, which was dissolved in a minimal amount of toluene and recrystallized at -35 °C. Crystals for X-ray diffraction studies were grown from the crude product oil at -35 °C. Yield: 136.0 mg (18%).

$^1$H NMR (400 MHz, C$_6$D$_6$): δ 7.66 (d, $J = 8.0$ Hz, 1H), 7.54 (dd, $J = 7.0$, 2.0 Hz, 1H), 7.46-7.43 (m, 3H), 7.25-7.20 (m, 3H), 7.19-7.13 (m, C$_6$D$_6$, 7H), 7.03 (dd, $J = 7.0$, 2.0 Hz, 1H), 3.24 (s, 1H), 2.70 (s, 1H), -0.07 (s, 9H), -0.59 (s, 9H)

$^{13}$C{$^1$H} NMR (101 MHz, C$_6$D$_6$): δ 144.32, 142.76, 140.12, 138.08, 130.77, 130.61, 129.53, 129.09, 128.96, 128.59, 127.54, 127.42, 126.00, 125.03, 49.78, 37.75, 0.61, 0.38

$^{11}$B NMR (128 MHz, C$_6$D$_6$): δ 75.4
FT-IR (cm$^{-1}$ (ranked intensity)): 2954 (10), 1695 (5), 1596 (8), 1473 (14), 1436 (12), 1311 (9), 1247 (2), 1197 (11), 1026 (6), 834 (1), 749 (3), 700 (4), 579 (13), 499 (7), 479 (15)

High-resolution mass spectrometry (HRMS) chemical ionization (CI): calcd for C$_{26}$H$_{33}$BSi$_{2}$ [M]$^+$, 412.2214; found, 412.2218.
Figure S-1: $^1$H NMR spectrum of 3 in C$_6$D$_6$. 
Figure S-2: Expansion of $^1$H NMR spectrum of 3 in C$_6$D$_6$ (aryl region).
Figure S-3: $^{13}$C-$^1$H NMR spectrum of 3 in C$_6$D$_6$. 
Figure S-4: Expansion of $^{13}\text{C}^{1}\text{H}$ NMR spectrum of 3 in C$_6$D$_6$ (aryl region).
Figure S-5: $^{11}$B NMR spectrum of 3 in C₆D₆.
Figure S-6: FT-IR spectrum of 3.
Figure S-7: High resolution mass spectrum of 3.
Figure S-8: $^1$H NMR spectrum of 4 in C$_6$D$_6$ (* indicates grease).
Figure S-9: Expansion of $^1$H NMR spectrum of 4 in C$_6$D$_6$ (aryl region).
Figure S-10: Expansion of $^1$H NMR spectrum of 4 in C$_6$D$_6$ (aliphatic region, * indicates grease).
Figure S-11: $^{13}\text{C}\{^{1}\text{H}\}$ NMR spectrum of 4 in C$_6$D$_6$ (* indicates grease).
Figure S-12: Expansion of $^{13}C\{^1H\}$ NMR spectrum of 4 in C$_6$D$_6$ (aryl region).
Figure S-13: $^{11}$B NMR spectrum of 4 in C$_6$D$_6$. 

![NMR spectrum of 4 in C$_6$D$_6$.](image)
Figure S-14: FT-IR spectrum of 4.
Figure S-15: High resolution mass spectrum of 4.
Table S-1: X-ray crystallographic details for 3 and 4.

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<td>c (Å)</td>
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<td>Radiation λ (Å)</td>
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<td>GOF (S)$^a$</td>
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<td>1.056</td>
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</table>

$^a$R1(F[I > 2(σI)]) = \sum |F_o| - |F_c|/\sum |F_o|; \ wR2(F^2 [all data]) = [w(F_o^2 - F_c^2)^2]^{1/2}; \ S(\text{all data}) = [w(F_o^2 - F_c^2)^2/(n-p)]^{1/2} (n = no. of data; p = no. of parameters varied; w = 1/[2/(F_o^2) + (aP)^2 + bP]) where P = (F_o^2 + 2F_c^2)/3 and a and b are constants suggested by the refinement program.
Figure S-16: Diagram of 4 illustrating the dihedral planes $\theta_{\text{prow}}$ and $\theta_{\text{stern}}$ defining the deviation of the ring from planarity into a boat-like conformation.

$\theta_{\text{stern}} = 43.71(13)^\circ$

$\theta_{\text{prow}} = 56.90(17)^\circ$
References

