Supplementary Data for:

A Chelated Borinium Cation

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General Considerations

All reactions and work-up procedures were performed under an inert atmosphere of dry, oxygen-free N₂, using standard Schlenk techniques or a glovebox (Vac, equipped with a -35 °C freezer) unless otherwise specified. DCM, n-pentane, n-hexane, Et₂O, and toluene (Sigma-Aldrich) were dried using a Grubbs-type Innovative Technologies solvent purification system, degassed, and stored over activated 3 or 4Å molecular sieves. Deuterated solvents (C₆D₆, CDCl₃, C₆D₅Br) were purchased from Cambridge Isotope Laboratories, Inc. or Sigma-Aldrich, and stored over activated 4Å molecular sieves prior to use, unless otherwise specified. Boron trifluoride diethyl etherate was purchased from Alfa Aesar. {DippNHSiMe₂CH₂}₂ 1 was generated according to a literature procedure.

Routine NMR spectra were obtained on a Varian MercuryPlus 300 MHz, Bruker Avance III 400 MHz, Agilent DD2 500 MHz, or Agilent DD2 600 MHz spectrometer and spectra were referenced to residual solvent of CDCl₃ (1H = 7.26; 13C = 77.2), C₆D₆ (1H = 7.16 ppm; 13C = 128.06 ppm), C₆D₅Br (1H most downfield shift = 7.30 ppm) or externally (¹¹B, BF₃·OEt₂; ¹⁹F, CFCl₃; ³¹P, 85% H₃PO₄). ¹³C spectra were primarily obtained on a 500 MHz Agilent DD2 NMR Spectrometer, equipped with a cryogenically cooled probe. Chemical shifts (δ) are reported in ppm and coupling constants are listed in Hz. High-resolution mass spectra (HRMS) were obtained on an Agilent 6538 Q-TOF (ESI), JEOL AccuTOF Plus 4G (DART) and Bruker Autoflex Speed (MALDI).
**X-ray Crystallography** Crystals were coated in Paratone-N oil in an N2 filled glovebox, brought out of the glovebox, mounted on a MiTegen Micromount, and placed under a cold N2 stream to maintain a dry, O2-free environment for each crystal during data collection. All data were collected on a Bruker Kappa Apex II diffractometer using a graphite monochromator with Mo kα radiation (λ = 0.7103 Å). Data were collected at 150 K for all crystals. A semi-empirical absorption correction was applied to the diffraction data using SADABS. We used Olex2 with an implementation of SHELX. This provides both SHELX and Olex2 solution and refinement options. The structures were solved by direct methods and refined by full-matrix least-squares on F2 using XL. All non-hydrogen atoms were refined anisotropically. Carbon-bound hydrogen atoms were placed in calculated positions using an appropriate riding model and coupled isotropic temperature factors. Descriptions of the refinement anomalies, where present, are given below. Further details can be found in the form of cif files available from the CCDC.

In the case of compound 8, repeated attempt to grow high quality crystals and collect X-ray data failed to give crystals in which disorder was absent. One of the ion pairs of the two in the asymmetric units exhibited disorder in an adamantyl group of the cation and in one of the C6F5 groups of the anion. However, as the primary purpose of the crystallographic study was to confirm the formulation of the compound, we feel it is appropriate to report this data while avoiding a detailed consideration of the metric parameters.

**Synthesis of ((Ad)NHSi(Me)2CH2)2**

\[
\text{NH}_2 \quad \xrightarrow{1) \text{n-BuLi, Et}_2\text{O}} \quad \text{NHN} \quad \text{Si} \quad \text{Si} \quad \text{NH} \quad \text{N}
\]

In 10 mL of pentane, 0.5000 g (3.306 mmol) of 1-AdNH₂ was dissolved before cooling to -25 °C. A 2.5 M hexane solution of n-BuLi (1.3 mL, 3.30 mmol) was added and the reaction was allowed to stir overnight, yielding a white precipitate. After settling, the pentane was decanted, and the solids were washed twice with 10 mL of pentane. The solid amide was suspended in 10 mL of Et₂O and cooled to -25 °C. A solution of 0.36 g (1.65 mmol) of (ClSi(Me)₂CH₂)₂ was prepared in a minimum volume of cold Et₂O (approximately 5 mL) and slowly added to the amide suspension. This was allowed to stir overnight. Celite was added to the resultant suspension and stirred before filtering. The solids were washed with 3 x 10 mL portions of Et₂O. After removing volatiles, solids were stirred with 10 mL of pentane and filtered, followed by two 10 mL washes of pentane. The volume was reduced in vacuo and the solution cooled at -25 °C to furnish 0.12 g (0.26 mmol, 16%) crystals of product, contaminated with some (1-Ad)N(Si(Me)₂CH₂)₂. The major product isolated when generating of 2 could be isolated by fractional crystallization.
1H NMR (400 MHz, Benzene-d6) δ 1.94 (s, 3H), 1.87 (d, J = 2.9 Hz, 6H), 1.53 (t, J = 3.0 Hz, 6H), 0.79 (s, 4H), 0.29 (s, 12H).

Figure S1 1H NMR spectrum of 2 in C₆D₆ at 298 K.

Figure S2. 1H NMR spectrum of 2 in CDCl₃ at 298 K.

Synthesis of ((Dipp)NSi(Me)₂CH₂)₂BF₃

![Synthesis reaction](image)
In 3 mL of toluene, 0.3406 g (0.685 mmol) of \{HN\textit{DippSi(Me)}\textsubscript{2}CH\textsubscript{2}\}\textsubscript{2} was dissolved and cooled. With stirring, 0.56 mL of a 2.5 M solution of \textit{n}-BuLi in hexane (1.405 mmol) was slowly added. This was stirred for 90 minutes before cooling again to -25 °C. While stirring in cold well, 88.8μL of BF\textsubscript{3}·OEt\textsubscript{2} was rapidly added. Stirring overnight gave a large amount of precipitate.

The above mixture was decanted, filtered and solids extracted with 2 x 2 mL portions of pentane. Solvent was removed \textit{in vacuo}. From this crude solid, the product was extracted with 3 x 2 mL portions of pentane. Contraction of the solvent caused spontaneous growth of 100 mg of white crystalline product. 45.6 mg of additional product could be isolated by decanting the solvent and cooling to -25 °C. The combined yield was 0.277 mmol (41%). \textsuperscript{1}H NMR (400 MHz, C\textsubscript{6}D\textsubscript{6}) δ 7.11 – 7.06 (m, 2H), 7.06 – 7.02 (m, 4H), 3.59 (hept, \textit{J} = 6.9 Hz, 4H), 1.29 (d, \textit{J} = 6.9 Hz, 13H), 1.20 (d, \textit{J} = 6.8 Hz, 13H), 0.99 (s, 4H), 0.09 (s, 12H). \textsuperscript{11}B NMR (128 MHz, C\textsubscript{6}D\textsubscript{6}) δ 23.9. \textsuperscript{13}C NMR (126 MHz, C\textsubscript{6}D\textsubscript{6}) δ 146.61, 141.09, 141.07, 126.73, 124.34, 28.96, 26.00, 25.98, 24.31, 12.17. \textsuperscript{19}F NMR (377 MHz, C\textsubscript{6}D\textsubscript{6}) δ -96.8, -96.9. MS (TOF, DART+) m/z 525.36715 (high res., calc. for [C\textsubscript{30}H\textsubscript{51}BN\textsubscript{2}F\textsubscript{2}Si\textsubscript{2}]\textsuperscript{+}: 525.36624)

**Figure S3** \textsuperscript{1}H NMR spectrum of 3 in C\textsubscript{6}D\textsubscript{6} at 298 K.
Figure S4 $^{11}$B NMR spectrum of 2 in C$_6$D$_6$ at 298 K.

Figure S5 $^{13}$C NMR spectrum of 3 in C$_6$D$_6$ at 298 K.
Figure S6. $^{19}$F NMR spectrum of 3 in $\text{C}_6\text{D}_6$ at 298 K.

Figure S7. $^{19}$F NMR spectroscopic identification of boron isotopes of 3. Coupled $^{19}$F (top), $^{19}$F{$^{10}$B} (middle), $^{19}$F{$^{11}$B} (bottom) in $\text{C}_6\text{D}_6$ at 298 K.
Figure S8. HR-MS (TOF DART+) data for molecular ion of 3, [C_{30}H_{51}BN_{2}FSi_{2}]^{+}.

Generation of \((\text{1-Ad})N(\text{Li(THF)})\text{HSi(Me)}_{2}\text{CH}_{2})_{2}\) 4

After lithiation of 2 in Et_{2}O with two equivalents of n-BuLi, an aliquot was removed, and solvent removed in vacuo. Crystals suitable for XRD were isolated from a THF solution of the reaction of 2 with n-BuLi dissolved in hexane. After stirring for three hours hexane was added and the mixture was filtered. Several crystals grew on standing at -25 °C.

\(^{1}H\) NMR 400 MHz, C_{6}D_{6} \delta 4.01 (br, int: 24.1, 24H), 2.06 (br, int: 5.0, 4H), 1.94 (br, int: 13.4, 12H), 1.65 (br, int: 13.2, 12H), 1.37 (br, int: 39.7, 36H), 0.95 (s, int: 5.3, 4H), 0.37 (s, int: 12.0, 12H).
Synthesis of ((1-Ad)NSi(Me)₂CH₂)₂BF₅

A 15 mL Et₂O solution of 0.224 g (0.503 mmol) of 2 was cooled to -25 °C, followed by dropwise addition of 0.43 mL of a 2.5 M solution of n-BuLi (1.06 mmol) in hexane, and stirred overnight. The solution was filtered. An aliquot was withdrawn and dried and subjected to NMR in C₆D₆. The aliquot was returned to the mother solution. The volume was contracted to one-third under vacuum, then doubled using pentane. This was repeated 3 times before contracting volume to approximately 3 mL and cooled to -25 °C. During this process, a large amount of precipitate formed. The solvent was decanted, and the precipitate was washed twice with 5 mL of pentane. Remaining solids were then redissolved in 10 mL of Et₂O and cooled, followed by dropwise addition of 62.1 μL (0.503 mmol) of BF₃·Et₂O with vigorous stirring. After stirring overnight, the mixture was filtered, and the solids washed with 2 x 2 mL Et₂O. Most of the volume was removed in vacuo before trituration with pentane. This was repeated, followed by removal of residual solvent to furnish 74.4 mg (0.157 mmol, 32%) of product as a white powder. Cooling a saturated pentane solution to -25 °C furnished crystals suitable for XRD.

¹H NMR (400 MHz, Benzene-d₆) δ 2.17 (d, J = 10.0 Hz, 12H), 1.99 (br, 12H), 1.68 – 1.50 (m, 12H), 0.97 (s, 2H), 0.80 (s, 2H), 0.41 (s, 12H). ¹¹B NMR (128 MHz, C₆D₆) δ 26.8. ¹³C NMR (126 MHz, C₆D₆) δ 55.81,
55.79, 44.68, 44.64, 36.86, 31.01, 14.12, 6.09. $^{19}$F NMR (377 MHz, C$_6$D$_6$) δ -71.4. MS (TOF, DART+) m/z 473.33503 (high res., calc. for protonated molecular ion, [C$_{25}$H$_{47}$BN$_2$FSi$_2$]$^+$: 473.33494); m/z 453.32805 (high res., calc. for borinium [B{1-AdNSiMe$_2$CH$_2$}]$_2$$^+$, [C$_{26}$H$_{46}$BN$_2$Si$_2$]$^+$: 453.32871)

**Figure S10** $^1$H NMR spectrum of 5 in C$_6$D$_6$ at 298 K.

**Figure S11** $^{11}$B NMR spectrum of 5 in C$_6$D$_6$ at 298 K.
Figure S12 $^{13}$C NMR spectrum of 5 in C$_6$D$_6$ at 298 K.

Figure S13 $^{19}$F NMR spectrum of 5 in C$_6$D$_6$ at 298 K.
Figure 14  $^{19}$F NMR spectroscopy identification of boron isotopes of 5. Coupled $^{19}$F spectrum (top), $^{19}$F{$^{10}$B} (middle), $^{19}$F{$^{11}$B} (bottom) in C$_6$D$_6$ at 298 K.
**Figure S15.** HR-MS (TOF, DART+) data for the molecular ion of 5, [C26H47BN2FSi2]⁺.
Figure S16. HR-MS (TOF, DART+) data for borinium [B((1-Ad)NSiMe₂CH₂)₂]⁺, [C₂₆H₄₆BN₂Si₂]⁺, via loss of F⁻ from 5.

**Generation of [((Dipp)NSi(Me)₂CH₂)₂BH 7**

63.3 mg (0.121 mmol) of 3 was dissolved in 0.2 mL of C₆D₅Br and 16.6 mg (0.143 mmol) of HSiEt₃ was added. 11.1 mg (0.012 mmol) of [Ph₃C][BArF] was dissolved in 0.1 mL of C₆D₅Br and added to the borane solution. The resulting yellow solution was transferred to an NMR tube and crude NMR spectroscopy indicated partial consumption of most 3, concurrent with generation of a new product with a broad ¹¹B chemical shift of 37 ppm. After 1h the reaction appeared to be complete. The solution was filtered. Pentane was added and the solution was stored at -25°C, yielding a yellow precipitate. The solution was filtered and the solid extracted with 2 x 1 mL portions of pentane several times resulting in a sticky oil. This was used for NMR spectroscopic studies.
$^1$H NMR (500 MHz, C$_6$D$_5$Br) δ 8.07 – 7.90 (m, 1H), 7.86 (d, $^3$J$_{H-H}$ = 8 Hz, 2H), 7.42 (s, 1H), 7.33 (t, $^3$J$_{H-H}$ = 8 Hz, 1H), 7.24 (t, $^3$J$_{H-H}$ = 8 Hz, 1H), 3.21 (hept, $^3$J$_{H-H}$ = 7 Hz, 3H), 2.83 – 2.71 (m, 2H), 1.13 (d, $^3$J$_{H-H}$ = 7 Hz, 3H), 1.05 (d, $^3$J$_{H-H}$ = 7 Hz, 3H), 1.04 (d, $^3$J$_{H-H}$ = 7 Hz, 3H), 0.87 – 0.82 (m, 6H), 0.80 – 0.72 (m, 4H), 0.22 (s, 6H), -0.19 (s, 6H).

$^{11}$B NMR (128 MHz, C$_6$D$_5$Br) δ 41.3, -16.6.

$^{19}$F NMR (377 MHz, C$_6$D$_5$Br) δ -131.68, -162.16 (t, $^3$J$_{F-F}$ = 20 Hz), -166.01 (t, $^3$J$_{F-F}$ = 20 Hz).

Figure S17 $^1$H NMR spectrum of 7 in C$_6$D$_5$Br at 298 K.
Figure S18. COSY $^1$H NMR spectrum of 7 in C$_6$D$_5$Br at 298 K.

Figure S19. $^{11}$B NMR spectrum of 7 in C$_6$D$_5$Br at 298 K.
Synthesis of [(1-Ad)NSi(Me)₂CH₂]₂B[B(C₆F₅)₄] 8

In ODFB, 0.156 mmol of [Et₃Si][B(C₆F₅)₄] was generated and triturated then washed twice with pentane. This was dissolved in 1 mL of ODFB, generating an orange solution, and was added to a stirred solution of 74.4 mg (0.157 mmol) of 5 in 1.5 mL of a 1:1 ODFB/pentane. On addition, colour changed to yellow, and the solution was stirred for 20 minutes before removing the solvent in vacuo. This was triturated with pentane followed by removal of solvent. Repeat until a viscous gel obtained. The crude material was redissolved in minimal DCM and triturate with pentane. After decanting and washing with 3 x 1 mL of pentane, the solids were dried in vacuo. This was recrystallized from DCM and pentane at -25° C, yielding 73.3 mg (0.06 mmol, 41%) of white, crystalline product. The decanted solvents were also contracted to give a small quantity of crude product, which can be recovered.

³¹H NMR (400 MHz, CDCl₃) δ 2.23 (s, 6H), 1.95 (d, ³J_H-H = 2.9 Hz, 12H), 1.81 – 1.72 (m, 6H), 1.68 – 1.60 (m, 6H), 1.15 (s, 1H), 0.72 – 0.39 (m, 15H). SiCH₃ and SiCH₂ protons could not be reliably integrated due to broadening.¹¹B NMR (128 MHz, CDCl₃) δ 34.2, -16.6.¹⁹F NMR (377 MHz, CDCl₃) δ -132.5, -163.2 (t, ³J_F-F = 20 Hz), -166.9 (t, ³J_F-F = 20 Hz).

After many attempts to grow single crystals and after collecting data from three separate crystals, we used the data from the best quality crystal to solve and the refine the presented structure. However, it is likely that the disorder in the adamantyl group and anion have had an

Figure S20. ¹⁹F NMR spectrum of 7 in C₆D₅Br at 298 K.
effect on the data from crystals of this material. Nonetheless we are confident that the data
does confirm connectivity of the compound.

Figure S21. $^1$H NMR spectrum of 8 in CDCl$_3$ at 298 K.

Figure S22. $^1$H COSY NMR spectrum of 8 in CDCl$_3$ at 298 K.
Figure S23. $^{11}$B NMR spectrum of 8 in CDCl$_3$ at 298 K.

Figure S24. $^{19}$F NMR spectrum of 8 in CDCl$_3$ at 298 K.