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Cyclic boronium and borenium cations derived from borabenzene-pyridine

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General Procedures. All manipulations were performed under argon atmosphere using standard glovebox and Schlenk techniques. Toluene and n-hexane solvents were dried and purified by passing through activated alumina and Q5 columns.1 Methylene dichloride was dried and distilled from CaH2. Pyridine was purchased from Aldrich Chemical Co. and distilled prior to use. Pyridine hydrochloride was prepared by adding a solution of HCl in Et2O to pyridine in Et2O at room temperature. A white precipitate forms immediately, which was washed with Et2O and dried under vacuum. 1-chloro-2-(trimethylsilyl)-4-(isopropyl)boracyclohexa-2,5-diene2, borabenzene lutidine3, borabenzene pyridine3 1a, and Tib(C6F5)44 were prepared according to reported procedures. 1-chloro-2-(trimethylsilyl)-4-(methyl)boracyclohexa-2,5-diene was prepared according to the synthetic procedure reported for 1-chloro-2-(trimethylsilyl)-4-(isopropyl)boracyclohexa-2,5-diene.2 All NMR spectra were performed in dry, oxygen-free CD2Cl2 or CDCl3. 1H, 13C{1H}, DEPT-135, 11B, COSY and HMQC NMR experiments were recorded on a Bruker DRX-400 spectrometer. 1H and 13C{1H} NMR spectra were calibrated using signals from the solvent and are reported downfield from SiMe4, whereas 11B NMR spectra are referenced to external BF3·OEt2.
Mass spectra were recorded on Esquire 3000, Kratos MS80RFA or Micromass VG7070 spectrometers. The pattern of boron-containing ions was compared with theoretical values.


**Synthesis of 1b.** Pyridine (227 mg, 0.23 mL, 2.87 mmol) was added dropwise to a stirred solution of 1-chloro-2-(trimethylsilyl)-4-(isopropyl)boracyclohexa-2,5-diene (650 mg, 2.87 mmol) in 10 mL toluene at room temperature. The solution was stirred for 1 h at room temperature, and the volatiles were removed under vacuum. The resulting solid was slurried in *n*-hexane, sonicated, and filtered to collect an orange solid (422 mg, 75%). Suitable crystals for X-ray diffraction study were grown by cooling a solution of 1b in CH₂Cl₂ at −35 °C. "H NMR (CD₂Cl₂, 400 MHz): δ 1.27 (d, 6H, CH₃-iPr, 3J_HH = 6.9 Hz), 2.87 (sept., 1H, CH-iPr, 3J_HH = 6.9 Hz), 6.63 (d, 2H, BCHCH, 3J_HH = 10.7 Hz), 7.34 (d, 2H, BCHCH, 3J_HH = 10.4 Hz), 7.68 (dd, 2H, C₆H₅-meta, 3J_HH = 6.9 Hz), 8.01 (t, 1H, C₆H₅-para, 3J_HH = 7.6 Hz), 9.00 (d, 2H, C₆H₅-ortho, 3J_HH = 5.4 Hz). "C{"H} NMR (CD₂Cl₂, 100 MHz): δ 25.60 (s, CH₃-iPr), 35.30 (s, CH-iPr), 118.99 (s, br, BCHCH), 126.86 (s, C₆H₅-meta), 133.66 (s, BCHCH), 136.18 (s, C-ipso), 140.46 (s, C₆H₅-para), 144.54 (s, C₆H₅-ortho). "B NMR (CD₂Cl₂, 128 MHz): δ 31.80 (s). EI-MS: m/z: 197 [M⁺], 182 [M⁺ - CH₃], 154 [M⁺ - CH(CH₃)₂]. EI-HRMS: 197.13644 (calcd 197.13758 amu, C₁₃H₁₆BN).

**Synthesis of 1c.** Pyridine (0.77 g, 0.79 mL, 9.74 mmol) was added dropwise to a stirred solution of 1-chloro-2-(trimethylsilyl)-4-(methyl)boracyclohexa-2,5-diene (1.95 g, 9.82 mmol) in 50 mL hexane at room temperature. The solution was stirred for 1 h at room temperature, and the volatiles were removed under vacuum. The resulting solid was slurried in *n*-hexane, sonicated, and filtered to collect an orange solid (1.53 g, 92%). "H NMR (CD₂Cl₂, 400 MHz): δ 2.36 (s, 3H, CH₃), 6.62 (d, 2H, BCHCH(Me), 3J_HH = 10.6 Hz), 7.30 (d, br, 2H, BCHCH(Me), 3J_HH = 10.1 Hz), 7.64 (m, 2H, C₆H₅-meta), 7.98 (dt,
Synthesis of [2a]Cl and [3a]Cl. A suspension of pyridine hydrochloride (149 mg, 1.29 mmol) in 5 mL of CH₂Cl₂ was added dropwise to a solution of borabenzene pyridine (200 mg, 1.29 mmol) in 5 mL of CH₂Cl₂ at room temperature. The solution was stirred for 15 min at room temperature, and the volatiles were removed under vacuum to leave 348 mg (100 %) of a white solid. The compound was obtained as a 1:1 mixture of two regioisomers. Cooling a solution containing [2a]Cl and [3a]Cl in CH₂Cl₂ at –35 ºC gave suitable crystals for X-ray diffraction study of the 2,5-isomer [3a]Cl. ¹H NMR (CD₂Cl₂, 400 MHz, -30 ºC): δ 2a 1.93 (dd, br, 2H, BCH₂CHCH, ³JHH = 4.4 Hz, ⁴JHH = 1.4 Hz), 5.76 (m, 1H, BCH₂CH), 5.85 (m, 1H, BCH₂CHCH), 6.29 (d, 1H, BCHCH₂CH, ³JHH = 12.0 Hz), 6.50 (dd, 1H, BCHCH₂CH, ³JHH = 12.5 Hz, ³JHH = 4.8 Hz), 7.90 (m, 4H, C₅H₅N-meta), 8.30 (m, 2H, C₅H₅N-para), 8.74 or 8.89 (m, 4H, C₅H₅N-ortho). ³C{¹H} NMR (CD₂Cl₂, 100 MHz, -30 ºC): δ 2a 22.10 (s, br, BCH₂CH), 125.11 (s, BCH₂CH₂CH), 127.01 or 127.14 (s, C₅H₅N-meta), 129.27 (s, BCH₂CHCH), 130.30 (s, br, BCH₂CH₂CH), 136.48 (s, BCH₂CH), 140.13 (s, BCH₂CH₂CH), 143.05 or 143.17 (s, C₅H₅N-para), 130.30 (s, br, BCH₂CH₂CH), 143.05 or 143.17 (s, C₅H₅N-para), 144.95 (s, C₅H₅N-ortho). ¹¹B NMR (CD₂Cl₂, 128 MHz, -30 ºC): δ 2a 4.82 (s), 3a 0.36 (s). ESI-MS: m/z: 156 [2a,3a - C₅H₅N]+, 77 [2a,3a – 2C₅H₅N]+.

Synthesis of [2b]Cl. A suspension of pyridine hydrochloride (59 mg, 0.51 mmol) in 2 mL of CH₂Cl₂ was added dropwise to a solution of 1b (100 mg, 0.51 mmol) in 4 mL of CH₂Cl₂ at room temperature. The solution was stirred for 15 min at room temperature,
and the volatiles were removed under vacuum to leave 158 mg (100 %) of a white solid.  

$^1$H NMR (CD$_2$Cl$_2$, 400 MHz, -50 °C): δ 0.89 (d, 6H, CH$_3$-Pr, $^3$J$_{HH} = 6.8$ Hz), 1.92 (d, 2H, BCH$_2$CHC(Pr), $^3$J$_{HH} = 4.6$ Hz), 2.21 (sept., 1H, CH-Pr, $^3$J$_{HH} = 6.7$ Hz), 5.60 (t, 1H, BCH$_2$CHC(Pr), $^3$J$_{HH} = 4.8$ Hz), 6.21 (d, 1H, BCHCHC(Pr), $^3$J$_{HH} = 12.4$ Hz), 6.57 (d, 1H, BCHCHC(Pr), $^3$J$_{HH} = 12.4$ Hz), 7.88 (dd, 4H, C$_5$H$_5$N-meta, $^3$J$_{HH} = 6.8$ Hz), 8.27 (t, 2H, C$_5$H$_5$N-para, $^3$J$_{HH} = 7.7$ Hz), 8.71 (d, 4H, C$_5$H$_5$N-ortho, $^3$J$_{HH} = 5.4$ Hz).  

$^{13}$C{$^1$H} NMR (CD$_2$Cl$_2$, 100 MHz, -50 °C): δ 21.17 (s, C$_7$H$_3$-iPr), 22.11 (s, br, BCH$_2$CHC(Pr)), 33.41 (s, C$_7$H$_7$-iPr), 120.24 (s, BCH$_2$CHC(Pr)), 127.20 (s, C$_5$H$_5$N-meta), 130.63 (s, br, BCHCHC(Pr)), 139.63 (s, BCHCHC(Pr)), 142.41 (s, BCHCHC(Pr)), 143.35 (s, C$_5$H$_5$N-para), 144.92 (s, C$_5$H$_5$N-ortho).  

$^{11}$B NMR (CD$_2$Cl$_2$, 128 MHz, -50 °C): δ 5.10 (s, br).  

ESI-MS: m/z: 198 [2b - C$_5$H$_5$N]+, 156 [C$_5$H$_6$B-C$_5$H$_5$N]+.

**Synthesis of 4a and 5a.** A solution of borabenzene pyridine (100 mg, 0.64 mmol) in 6 mL CH$_2$Cl$_2$ was treated with HCl gas (23 mg, 63 mmol) at –78 °C. The color of the solution changed immediately from orange to colorless. After 10 min the volatiles were removed in vacuum to leave 123 mg (100 %) of a colorless oil. The compound was obtained as a 1:1 mixture of two regioisomers.  

$^1$H NMR (C$_6$D$_6$, 400 MHz, 25 °C): δ 21.17 (s, CH$_3$-Pr), 22.11 (s, br, BCH$_2$CHC(Pr)), 33.41 (s, CH$_2$-Pr), 120.24 (s, BCH$_2$CHC(Pr)), 127.20 (s, C$_5$H$_5$N-meta), 130.63 (s, br, BCHCHC(Pr)), 139.63 (s, BCHCHC(Pr)), 142.41 (s, BCHCHC(Pr)), 143.35 (s, C$_5$H$_5$N-para), 144.92 (s, C$_5$H$_5$N-ortho).  

$^{13}$C{$^1$H} NMR (C$_6$D$_6$, 100 MHz, 25 °C): δ 28.61 (s, br, BCH$_2$CHC(Pr)), 125.37 (s, C$_5$H$_5$N-meta), 125.68 (s, BCH$_2$CHC(Pr)), 133.60 (s, BCHCHC(Pr)), 135.36 (s, BCH$_2$CHC(Pr)), 136.37 (s, br, BCHCHC(Pr)), 140.64 (s, C$_5$H$_5$N-para), 144.47 (s, C$_5$H$_5$N-ortho).  

$^{11}$B NMR (C$_6$D$_6$, 128 MHz, 25 °C): δ 4.89 (s), 1.13 (s). EI-MS: m/z: 112 [4a,5a - C$_5$H$_5$N]+, 79 [C$_5$H$_5$N]+.
Synthesis of 4b. A solution of 1b (105 mg, 0.53 mmol) in 8 mL CH2Cl2 was treated with HCl gas (22 mg, 60 mmol) at –78 °C. The color of the solution changed immediately from orange to colorless. After 10 min the volatiles were removed in vacuum to leave 124 mg (100 %) of a colorless oil. 1H NMR (C6D6, 400 MHz, 25 °C): δ 1.19 (d, 6H, C3H3-iPr, 3JHH = 6.8 Hz), 1.71 (d, br, 2H, BCH2CHC(iPr), 3JHH = 15.1 Hz), 2.47 (sept., 1H, C2H-iPr, 3JHH = 6.8 Hz), 5.83 (s, br, 1H, BCH2C(iPr)), 6.46 (d, 1H, BCHCHC(iPr), 3JHH = 12.2 Hz), 6.64 (dd, 2H, C5H5N-meta, 3JHH = 6.7 Hz), 6.70 (d, 1H, BCHC(iPr)), 6.99 (t, 1H, C5H5N-para, 3JHH = 7.5 Hz), 8.69 (d, br, 2H, C5H5N-ortho, 3JHH = 4.5 Hz). 13C{1H} NMR (C6D6, 100 MHz, 25 °C): δ 22.21 (s, br, C3H3-iPr), 22.31 (s, br, C3H3-iPr), 28.13 (s, br, BC3H2CHC(iPr)), 34.66 (s, C3H-iPr), 122.05 (s, BCH2C(iPr)), 125.19 (s, C5H5N-meta), 136.05 (s, BCHCHC(iPr)), 136.99 (s, br, BC3H2CHC(iPr)), 140.41 (s, C5H5N-meta), 142.11 (s, BCHCHC(iPr)), 144.47 (s, br, C5H5N-ortho). 11B NMR (C6D6, 128 MHz, 25 °C): δ 5.08 (s, br). EI-MS: m/z: 119 [4b - C5H5N, - Cl]+, 104 [4b - C5H5N, - Cl, -CH3]+, 79 [C5H5N]+.

Synthesis of 4c. A solution of 1c (150 mg, 0.88 mmol) in 10 mL CH2Cl2 was treated with HCl gas (32 mg, 0.88 mmol) at –78 °C. The color of the solution changed immediately from orange to colorless. After 10 min the volatiles were removed in vacuum to leave 182 mg (100 %) of a colorless oil. 1H NMR (CD2Cl2, 400 MHz, 25 °C): δ AB spin system: A 1.46 (d, br., 1H, BC3H2CHC(CH3), 2JHH = 18.8 Hz), B 1.88 (d, br., 1H, BCH2CHC(CH3), 2JHH = 18.8 Hz), 1.76 (m, 3H, BCH2CHC(CH3)), 5.57 (s, br, 1H, BCH2CHC(CH3)), 6.00 (d, 1H, BCHCHC(CH3), 3JHH = 12.0 Hz), 6.31 (d, br., 1H, BCHCHC(CH3), 3JHH = 12.0 Hz), 7.66 (dd, 2H, C5H5N-meta, 3JHH = 7.08 Hz), 8.08 (t, 1H, C5H5N-para, 3JHH = 7.6 Hz), 8.89 (d, br, 2H, C5H5N-ortho, 3JHH = 5.2 Hz). 13C{1H} NMR (CD2Cl2, 100 MHz, 25 °C): δ 22.72 (s, br, BCH2CHC(CH3)), 27.49 (s, br, BCH2CHC(CH3)), 124.63 (s, BCH2CHC(CH3)), 126.27 (s, C5H5N-meta), 131.82 (s, BCHCHC(CH3)), 136.27 (s, br, BCHCHC(CH3)), 141.83 (s, C5H5N-meta), 145.26 (s, C5H5N-ortho). 11B NMR (CD2Cl2, 128 MHz, 25 °C): δ 4.75 (s, br). EI-MS: m/z: 170 [4c - Cl]+, 126 [4c - C5H5N]+, 111 [4c - C5H5N, - CH3]+, 79 [C5H5N]+.
Synthesis of 6a and 7a. A solution of TIB(C₆F₅)₄ (203 mg, 0.23 mmol) in 5 mL CH₂Cl₂ was added dropwise to a solution containing a mixture of 4a and 5a (44 mg, 0.23 mmol) in 4 mL CH₂Cl₂ and stirred for 10 min at room temperature. The white precipitate of TICl was removed by filtration. The compound was obtained as a mixture of 2,5- and 2,4-isomers in 9:1 ratio, after recrystallization from CH₂Cl₂/hexane: yield 123 mg (64 %). ¹H NMR (CD₂Cl₂, 400 MHz, 25 °C): 7a 3.78 (m, 2H, BCHCHC₃H₂), 7.01 (dt, 2H, BC₃HCHCH₂, 3 JHH = 12.0 Hz, 4 JHH = 1.2 Hz), 8.21 (m, 4H, BCHCHCH₂ + C₅H₅N-meta), 8.73 (m, C₅H₅N-para), 9.1 (d, 2H, C₅H₅N-ortho, 3 JHH = 5.3 Hz). 6a 2.89 (d, br, 2H, BC₃H₂CHCH, 3 JHH = 3.5 Hz), 6.09 (dt, 1H, BCH₂CHC₃H, 3 JHH = 1.7Hz, 3 JHH = 12.7Hz), 6.73 (d, br, 1H, BCHCHCH, 3 JHH = 12.2 Hz), 6.93 (1H, BCHCHC₃H), 8.27 (m, 2H, C₅H₅N-meta, partially overlapping with the C₅H₅N-meta signal of 7a), 8.78 (m, 2H, C₅H₅N-para, partially overlapping with the C₅H₅N-para signal of 7a), 9.02 (d, 2H, C₅H₅N-ortho, 3 JHH = 5.2 Hz). ¹³C{¹H} NMR (CD₂Cl₂, 100 MHz, 25 °C): 7a δ 40.47 (s, BCHCHC₃H₂), 124.81 (s, br, B₃C₅H₅), 128.18 (s, C- ipso), 129.24 (s, C₅H₅N-meta), 136.90 (d, br, C₆F₅-meta, 1 JCF = 244.9 Hz), 138.82 (d, C₆F₅-para, 1 JCF = 244.0 Hz), 146.09 (s, C₅H₅N-ortho), 148.10 (d, C₅F₅-ortho, 1 JCF = 239.0 Hz), 150.15 (s, C₅H₅N-para), 168.77 (s, BCHCHCH₂) signals for the 6a isomer were not detected. ¹¹B NMR (CD₂Cl₂, 128 MHz, 25 °C): 7a δ -17.43 (s, B(C₆F₅)₄) 45.52 (s, br, BC₃H₂) 6a δ -17.43 (s, B(C₆F₅)₄) 57.24 (s, br, BC₃H₅). ¹⁹F NMR (CD₂Cl₂, 282 MHz, 25 °C): δ -167.20 (dd, C₆F₅-meta, 3 JFF = 28.2 Hz), -163.3 (t, C₆F₅-para, 3 JFF = 28.2 Hz), -133.00 (s, br, C₆F₅-ortho). ESI-MSpos: m/z: 156 [6a,7a - B(C₆F₅)₄], 80 [C₅N₅H]. ESI-MSneg: m/z: 679 [B(C₆F₅)₄].

Synthesis of 6b. A solution of TIB(C₆F₅)₄ (113 mg, 0.13 mmol) in 4 mL CH₂Cl₂ was added dropwise to a solution of 4b (30 mg, 0.13 mmol) in 2 mL CH₂Cl₂ and the mixture stirred for 10 min at room temperature. The white precipitate of TICl was removed by filtration. 6b was obtained as a white crystalline solid by layering a CH₂Cl₂ solution with hexane and allowing the two solvents to diffuse: yield 88 mg (78 %). ¹H NMR (CD₂Cl₂, 400 MHz, 25 °C): 6b 1.21 (d, 6H, C₃H₃-iPr, 3 JHH = 6.9 Hz), 2.75 (sept., 1H, CH₃-iPr, 3 JHH = 6.8 Hz), 2.85 (d, 2H, BCH₂CHC₃(Pr), 3 JHH = 4.1 Hz), 6.74 (s, br, 1H, BCH₂CHC(Pr),...
Synthesis of 6c. A solution of TlB(C₆F₅)₄ (176 mg, 0.20 mmol) in 4 mL CH₂Cl₂ was added dropwise to a solution of 4c (41 mg, 0.20 mmol) in 2 mL CH₂Cl₂ and the mixture stirred for 10 min at room temperature. The white precipitate of TlCl was removed by filtration. 6c was obtained as colorless crystals by layering a CH₂Cl₂ solution with hexane and allowing the two solvents to diffuse: yield 122 mg (72 %). ¹H NMR (CD₂Cl₂, 400 MHz, 25 °C): δ 2.18 (m, 3H, C₃H₃), 2.83 (d, br, 2H, BCH₂CHC(CH₃)), 6.73 (s, br, 1H, BCH₂CHC(CH₃)), 6.88 (d, 1H, BCHCH(CH₃), 3JHH = 12.0 Hz), 8.14 (d, br, 1H, BCHCH(CH₃), 3JHH = 12.0 Hz), 8.18 (m, 2H, C₅H₅N-meta), 8.18 (m, 2H, C₅H₅N-meta), 124.86 (s, br, BCH₂CHC(CH₃)), 129.37 (s, C₅H₅N-meta), 139.91 (d, C₆F₅-meta, 1JCF = 244.2 Hz), 137.67 (s, BCH₂CHC(CH₃)), 138.86 (d, C₆F₅-para, 1JCF = 237.7 Hz), 145.71 (s, C₅H₅N-ortho), 148.73 (d, C₆F₅-ortho, 1JCF = 240.3 Hz), 150.39 (s, C₅H₅N-para), 169.67 (s, BCHCH(CH₃)). C-ipso was not detected. ¹¹B NMR (CD₂Cl₂, 128 MHz, 25 °C): δ -17.28 (s, B(C₆F₅)₄), 56.39 (s, br, B(C₆F₅)₄). ¹⁹F NMR (CD₂Cl₂, 282 MHz, 25 °C): δ -167.20 (dd, C₆F₅-meta, 3JFF = 28.2 Hz), -163.3 (t, C₆F₅-para, 3JFF = 28.2 Hz), -133.00 (s, br, C₆F₅-ortho). ESI-MS pos: m/z: 198 [6b - B(C₆F₅)₄]+, 155 [6b - B(C₆F₅)₄], -CH(CH₃)₂]+. ESI-MS neg: m/z: 679 [B(C₆F₅)₄]⁻.
Synthesis of [2a][B(C6F5)4] and [3a][B(C6F5)4]. TlB(C6F5)4 (114 mg, 0.13 mmol) in 2 mL of CH2Cl2 was added dropwise to a solution containing a mixture of [2a]Cl and [3a]Cl (35 mg, 0.13 mmol) in 2 mL of CH2Cl2 at room temperature. The solution was stirred for 15 min at room temperature. The white precipitate of TlCl was removed by filtration and the volatiles were removed under vacuum to leave 118 mg (100 %) of a white solid. The compound was obtained as a mixture of 2,5- and 2,4-isomers in 2:1 ratio.

$^1$H NMR (CD2Cl2, 400 MHz 25 °C): $\delta$ [2a][B(C6F5)4] 1.97 (d, br, 2H, BC\textsubscript{6}H\textsubscript{2}CHCH, $^3J_{HH} = 2.2$ Hz), 6.04 (m, 2H, BCH\textsubscript{2}CHCH + BCH\textsubscript{2}CHCH), 6.67 (m, 1H, BCHCH overlapping with signals from [3a][B(C6F5)4]), 6.86 (dd, 1H, BC\textsubscript{6}H\textsubscript{2}CHCH, $^3J_{HH} = 10.7$ Hz, $^4J_{HH} = 1.0$ Hz), 7.81 (m, 4H, C\textsubscript{5}H\textsubscript{5}N-\textsubscript{meta}), 8.28 (m, 2H, C\textsubscript{5}H\textsubscript{5}N-\textsubscript{para}), 8.45 (m, 4H, C\textsubscript{6}F\textsubscript{5}-\textsubscript{ortho}).

$^1$H NMR (CD2Cl2, 400 MHz 25 °C): $\delta$ [3a][B(C6F5)4] 2.93 (m, 2H, BCH\textsubscript{2}CHCH, $^3J_{HH} = 12.7$ Hz, $^4J_{HH} = 2.0$ Hz), 6.7 (d, br, BCH\textsubscript{2}CHCH, $^3J_{HH} = 12.4$ Hz), 7.81 (m, 4H, C\textsubscript{5}H\textsubscript{5}N-\textsubscript{meta}), 8.28 (m, 2H, C\textsubscript{5}H\textsubscript{5}N-\textsubscript{para}), 8.45 (m, 4H, C\textsubscript{6}F\textsubscript{5}-\textsubscript{ortho}).

$^{13}$C\{1H\} NMR (CD2Cl2, 100 MHz, 25 °C): $\delta$ [2a][B(C6F5)4] 24.60 (s, br, B\textsubscript{C}\textsubscript{6}H\textsubscript{2}CH), 126.69 (s, BCH\textsubscript{2}CHCH), 128.23 (s, C\textsubscript{6}F\textsubscript{5}-\textsubscript{meta}), 129.58 (s, BCH\textsubscript{2}CHCH), 136.91 (d, br, C\textsubscript{6}F\textsubscript{5}-\textsubscript{meta}, $^1J_{CF} = 244.3$ Hz), 138.85 (d, C\textsubscript{6}F\textsubscript{5}-\textsubscript{para}, $^1J_{CF} = 243.9$ Hz), 139.00 (s, BCH\textsubscript{2}CHCH), 144.45 (s, C\textsubscript{5}H\textsubscript{5}N-\textsubscript{meta}), 145.06 (s, C\textsubscript{5}H\textsubscript{5}N-\textsubscript{ortho}), 148.75 (d, C\textsubscript{6}F\textsubscript{5}-\textsubscript{ortho}, $^1J_{CF} = 238.4$ Hz). [3a][B(C6F5)4] 33.32 (s, BCH\textsubscript{2}CHCH), 124.27 (s, br, BCH\textsubscript{2}CHCH), 127.65 (s, C\textsubscript{6}F\textsubscript{5}-\textsubscript{meta}), 136.91 (d, br, C\textsubscript{6}F\textsubscript{5}-\textsubscript{meta}, $^1J_{CF} = 244.3$ Hz), 138.85 (d, C\textsubscript{6}F\textsubscript{5}-\textsubscript{para}, $^1J_{CF} = 243.9$ Hz), 142.70 (s, BCH\textsubscript{2}CHCH), 144.09 (s, C\textsubscript{5}H\textsubscript{5}N-\textsubscript{para}), 145.50 (s, C\textsubscript{5}H\textsubscript{5}N-\textsubscript{ortho}), 148.75 (d, C\textsubscript{6}F\textsubscript{5}-\textsubscript{ortho}, $^1J_{CF} = 238.4$ Hz).

$^{11}$B NMR (CD2Cl2, 128 MHz, 25 °C): $\delta$ [2a][B(C6F5)4] $\delta$ -17.43 (s, B(C\textsubscript{6}F\textsubscript{5})\textsubscript{4}), 5.09 (s, br, BC\textsubscript{5}H\textsubscript{5}). [3a][B(C6F5)4] $\delta$ -17.43 (s, B(C\textsubscript{6}F\textsubscript{5})\textsubscript{4}), 1.27 (s, br, BC\textsubscript{5}H\textsubscript{5}).

$^{19}$F NMR (CD2Cl2, 282 MHz, 25 °C): $\delta$ -167.20 (dd, C\textsubscript{6}F\textsubscript{5}-\textsubscript{meta}, $^3J_{FF} = 28.2$ Hz), -163.3 (t, C\textsubscript{6}F\textsubscript{5}-\textsubscript{para}, $^3J_{FF} = 28.2$ Hz), -133.00 (s, br, C\textsubscript{6}F\textsubscript{5}-\textsubscript{ortho}).

ESI-MSpos: m/z: 156 [2a,3a - C\textsubscript{6}N\textsubscript{5}]\textsuperscript{+}, 80 [C\textsubscript{6}N\textsubscript{5}H]\textsuperscript{+}, 77 [2a,3a - 2 C\textsubscript{6}N\textsubscript{3}]\textsuperscript{+}. ESI-MSneg: m/z: 679 [B(C\textsubscript{6}F\textsubscript{5})\textsubscript{4}]\textsuperscript{−}.
Synthesis of [2b][B(C6F5)4]. TlB(C6F5)4 (99 mg, 0.11 mmol) in 2 mL of CH2Cl2 was added dropwise to a solution of 3 (35 mg, 0.11 mmol) in 2 mL of CH2Cl2 at room temperature. The solution was stirred for 15 min at room temperature. The white precipitate of TlCl was removed by filtration and the volatiles were removed under vacuum to leave 107 mg (100 %) of a white solid. 1H NMR (C6D5Br, 300 MHz, 25 °C): δ 0.97 (d, 6H, CH3-iPr, 3JHH = 6.8 Hz), 1.58 (d, br, 2H, BCH2CHC(iPr), 3JHH = 4.5 Hz), 2.23 (sept., 1H, CH-iPr, 3JHH = 6.8 Hz), 5.58 (s, br, 1H, BCH2CHC(iPr)), 5.77 (d, 1H, BCHCHC(Pt), 3JHH = 12.3 Hz), 6.56 (d, 1H, BCHCHC(Pt), 3JHH = 12.3 Hz), 7.06 (dd, 4H, C5H5N-meta, 3JHH = 6.7 Hz), 7.48 (t, 2H, C5H5N-para, 3JHH = 7.5 Hz), 7.92 (d, br, 4H, C5H5N-ortho, 3JHH = 5.5 Hz). 13C{1H} NMR (C6D5Br, 75 MHz, 25 °C): δ 21.41 (s, CH3-iPr), 22.60 (s, br, BCH2CHC(iPr)), 33.64 (s, CH-iPr), 119.94 (s, BCH2CHC(iPr)), 126.62 (s, C5H5N-meta), 129.63 (s, BCHCHC(Pt), buried under the signal of C6D5Br), 136.30 (d, C6F5-meta, 1JCF = 242.0 Hz), 138.18 (d, C6F5-para, 1JCF = 246.3 Hz), 140.72 (s, BCHCHC(Pt)), 142.67 (s, C5H5N-para), 143.18 (s, C-ipsos), 143.59 (s, C5H5N-ortho), 143.97 (s, C-ipsos), 148.35 (d, C6F5-ortho, 1JCF = 241.9 Hz). 11B NMR (C6D5Br, 96 MHz, 25 °C): δ -16.99 (s, B(C6F5)4), 5.13 (s, br, BC5H5). 19F NMR (CD2Cl2, 282 MHz, 25 °C): δ -167.30 (dd, C6F5-meta, 3JFF = 28.2 Hz), -163.4 (t, C6F5-para, 3JFF = 28.2 Hz), -133.00 (s, br, C6F5-ortho). ESI-MSpos: m/z: 198 [2b - Py]+, 156 [2b - Py, - C(CH3)2]+. ESI-MSneg: m/z: 679 [B(C6F5)4].