# **Electronic Supplementary Information**

# SET Processes in Lewis Acid-Base Reactions: the Tritylation

# of N-Heterocyclic Carbenes

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# **Experimental Part**

**General.** All reactions were performed under a controlled dry nitrogen atmosphere using a high-vacuum line, standard Schlenk techniques, and an MBraun glovebox. The used glassware was dried in an oven at 130 °C and evacuated prior to use. The solvents THF, diethyl ether (Et<sub>2</sub>O), benzene, toluene and *n*-pentane were dried by using an innovation technology SPS solvent system. Deuterated  $[D_2]$ dichloromethane (CD<sub>2</sub>Cl<sub>2</sub>) was dried by storing over molecular sieve (4 Å) for at least one day before degassing by three freeze-pump-thaw cycles. Standard chemicals were obtained from commercial suppliers and used as delivered if not mentioned otherwise. N-Heterocyclic carbenes were synthesized according to literature procedures.<sup>S1</sup>

**NMR spectroscopy.** NMR spectra were recorded on Bruker Avance DPX-400 spectrometers. <sup>1</sup>H NMR spectra were calibrated against the residual proton signal of the solvent as internal reference  $([D_2]$ dichloromethane:  $\delta$  <sup>1</sup>H(CDHCl<sub>2</sub>) = 5.32) and <sup>13</sup>C{<sup>1</sup>H} NMR spectra by using the central line of the solvent signal  $([D_2]$ dichloromethane:  $\delta$  <sup>13</sup>C(CDHCl<sub>2</sub>) = 53.8).

**Mass spectrometry.** High resolution mass spectra were recorded on an LTQ Orbitrap ELITE ETD with a nanoESI source, or a Xevo G2-S QTOF with an ESI source.

UV-vis spectroscopy. Data were recorded on a Cary 60 Spectrometer (Agilent Technologies).

**EPR Spectroscopy.** The EPR measurements were performed at room temperature using a Bruker EleXsys E500 X-band EPR spectrometer, which was equipped with a high-Q cylindrical cavity, Model ER 4122 SHQE (from Bruker BioSpin GmbH, Karlsruhe, Germany).

# Reaction of IDipp with [Ph<sub>3</sub>C][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] at -40 °C:



# Scheme S1.

A toluene solution (2 mL) of IDipp (1a) (100 mg, 0.257 mmol) was added slowly to a stirred toluene solution (2 mL) of  $[Ph_3C][B(C_6F_5)_4]$  (238 mg, 0.257 mmol) at -40 °C. The color of solution changed from orange to purple, and then to yellow. The resulting suspension was stirred for another 10 min. After that, the solvent was removed under vacuum, and the residue was washed three-times with *n*-pentane (3 x 4 mL). The resulting yellow solid was dried under vacuum (Yield: 330 mg, 98%). Light-yellow crystals of salt 2a, suitable for XRD analysis, were obtained from DCM / *n*-pentane (1:3) at -40 °C.

<sup>1</sup>H NMR (400 MHz, 298 K, [D<sub>2</sub>]dichloromethane):  $\delta = 1.24$  (d, <sup>3</sup>*J*(<sup>1</sup>H-<sup>1</sup>H) = 6.8 Hz, 12H, CH(C<u>H</u><sub>3</sub>)<sub>2</sub>), 1.35 (d, <sup>3</sup>*J*(<sup>1</sup>H-<sup>1</sup>H) = 6.8 Hz, 12H, CH(C<u>H</u><sub>3</sub>)<sub>2</sub>), 2.35 (sept., <sup>3</sup>*J*(<sup>1</sup>H-<sup>1</sup>H) = 6.8 Hz, 4H, C<u>H</u>(CH<sub>3</sub>)<sub>2</sub>), 4.76 (m, 1H, IDippC<u>H</u>), 5.35 (d of d, <sup>3</sup>*J*(<sup>1</sup>H-<sup>1</sup>H) = 4.0 Hz, 9.7 Hz, 2H, C<u>H</u>=CH), 6.40 (d of d, <sup>3</sup>*J*(<sup>1</sup>H-<sup>1</sup>H) = 2.0 Hz, 9.7 Hz, 2H, C<u>H</u>=CH), 6.89 (m, 4H, *o*-CPh<sub>2</sub>), 7.31 (m, 6H, *m*, *p*-CPh<sub>2</sub>), 7.47 (s, 2H, N-C<u>H</u>=CH), 7.50 (d, <sup>3</sup>*J*(<sup>1</sup>H-<sup>1</sup>H) = 7.9 Hz, 4H, *m*-Dipp), 7.73 (t, <sup>3</sup>*J*(<sup>1</sup>H-<sup>1</sup>H) = 7.9 Hz, 2H, *p*-Dipp).

<sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, 298 K, [D<sub>2</sub>]dichloromethane):  $\delta = 22.3$ , 26.1 (CH(<u>C</u>H<sub>3</sub>)<sub>2</sub>), 30.1 (<u>C</u>H(CH<sub>3</sub>)<sub>2</sub>), 36.8 (IDipp<u>C</u>H), 118.6 (<u>C</u>H=CH), 124.3 (<u>C</u>=CPh<sub>2</sub>), 125.6 (*m*-Dipp), 125.7 (N-<u>C</u>H=CH), 128.4 (*m*-C<u>Ph<sub>2</sub></u>), 128.5 (*p*-C<u>Ph<sub>2</sub></u>), 129.5 (*ipso*-Dipp), 130.4 (*o*-C<u>Ph<sub>2</sub></u>), 131.7 (<u>C</u>H=CH), 133.3 (*p*-Dipp), 136.8 (dm, <sup>1</sup>*J*(<sup>13</sup>C-<sup>19</sup>F) = 245 Hz, *m*-<u>C</u>-C<sub>6</sub>F<sub>5</sub>), 138.7 (dm, <sup>1</sup>*J*(<sup>13</sup>C-<sup>19</sup>F) = 245 Hz, *p*-<u>C</u>-C<sub>6</sub>F<sub>5</sub>), 140.5 (*ipso*-C<u>Ph<sub>2</sub></u>), 145.1 (C=<u>C</u>Ph<sub>2</sub>), 145.7 (*o*-Dipp), 147.2 (N<u>C</u>N), 148.6 (dm, <sup>1</sup>*J*(<sup>13</sup>C-<sup>19</sup>F) = 242 Hz, *o*-<u>C</u>-C<sub>6</sub>F<sub>5</sub>).

<sup>11</sup>B{<sup>1</sup>H} NMR (128 MHz, 298 K, [D<sub>2</sub>]dichloromethane):  $\delta = -16.6 (\underline{B}(C_6F_5)_4)$ .

<sup>19</sup>F{<sup>1</sup>H} NMR (377 MHz, 298 K, [D<sub>2</sub>]dichloromethane):  $\delta = -132.9$  (dm, *o*-C<u>F</u>), -163.5 (t, *p*-C<u>F</u>,  ${}^{3}J({}^{19}F-{}^{19}F) = 21$  Hz), -167.4 (t, *m*-C<u>F</u>,  ${}^{3}J({}^{19}F-{}^{19}F) = 18$  Hz).

HRMS (APPI/QTOF) m/z:  $[M]^+$  Calcd for  $C_{46}H_{51}N_2^+$  631.4047; Found 631.4040.

HRMS (APPI/QTOF) m/z: [M]<sup>-</sup> Calcd for C<sub>24</sub>BF<sub>20</sub><sup>-</sup> 678.9779; Found 678.9778.



Figure S1a. <sup>1</sup>H NMR (400 MHz, 298 K, [D<sub>2</sub>]dichloromethane) spectrum of 2a.



Figure S1b. <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, 298 K, [D<sub>2</sub>]dichloromethane) spectrum of 2a.



Figure S1c.  ${}^{11}B{}^{1}H$  NMR (128 MHz, 298 K, [D<sub>2</sub>]dichloromethane) spectrum of 2a.



Figure S1d. <sup>19</sup>F{<sup>1</sup>H} NMR (377 MHz, 298 K, [D<sub>2</sub>]dichloromethane) spectrum of **2a**.



# Reaction of IDipp with [Ph<sub>3</sub>C][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] at room temperature:

#### Scheme S2.

A toluene solution (2 mL) of IDipp (1a) (100 mg, 0.257 mmol) was added to a stirred toluene solution (2 mL) of  $[Ph_3C][B(C_6F_5)_4]$  (238 mg, 0.257 mmol) at room temperature. The color of solution changed from orange to purple, and then to brown (see the picture in Scheme S2). The resulting reaction mixture was stirred for another 1 h. After that, the solvent was removed under vacuum, and the light-yellow solid was used for NMR spectroscopy without purification. <sup>1</sup>H NMR spectroscopy indicated that the formation of adduct **2a** and **3a** in a ratio of 1 : 3.2 along with trace of Ph<sub>3</sub>CH (see Figure S2a).



**Figure S2a.** <sup>1</sup>H NMR (400 MHz, 298 K,  $[D_2]$ dichloromethane) spectrum of the products formed by reaction of IDipp with  $[Ph_3C][B(C_6F_5)_4]$  in toluene at room temperature.



**Figure S2b.** Stacked <sup>1</sup>H NMR (400 MHz, 298 K, [D<sub>2</sub>]dichloromethane) spectra of the reaction mixture, of adduct **2a**, of the imidazolium salt **3a**, of carbene **1a**, and of triphenyl methane (from the top to the bottom).



Figure S3. ESI-MS spectrum of the products formed by reaction of IDipp with  $[Ph_3C][B(C_6F_5)_4]$  in toluene at room temperature.



**Figure S4.** MS spectrum from a GC analysis of the products formed by reaction of IDipp with  $[Ph_3C][B(C_6F_5)_4]$  in toluene at room temperature (top), and NIST Mass Spectrometry Data Center spectrum of Ph<sub>3</sub>CH (bottom).



**Figure S5.** Color of a solution of  $[Ph_3C][B(C_6F_5)_4]$  in chlorobenzene upon dropwise addition of a chlorobenzene solution of IDipp (2 x 10<sup>-4</sup> M).



**Figure S6.** Black: Experimental EPR spectrum of the trityl radical in chlorobenzene (T = 298 K). The spectrum was recorded using the solution obtained after reaction of  $[Ph_3C][B(C_6F_5)_4]$  with IDipp in toluene at room temperature. Red: Simulated EPR spectrum of the trityl radical using the following parameters from the literature<sup>S2</sup>: g = 2.0025, A(o-H) = 2.6 G, A(m-H) = 1.1 G, A(p-H) = 2.8 G).



Figure S7. Evolution of the UV-vis spectra of a chlorobenzene solution containing 1a and  $[Ph_3C][B(C_6F_5)_4]$  (2 x 10<sup>-4</sup> M). The spectra were collected during 5 min.



**Figure S8.** Evolution of the UV-vis spectra of the reaction mixture of **1a** with  $[Ph_3C][B(C_6F_5)_4]$  in chlorobenzene after being exposed to air (2 x 10<sup>-4</sup> M).



Figure S9. UV-vis spectrum of adduct 2a in chlorobenzene (10<sup>-4</sup> M).



Figure S10. UV-vis spectrum of salt  $[Ph_3C][B(C_6F_5)_4]$  in chlorobenzene  $(10^{-4} \text{ M})$ .



**Figure S11.** Evolution of the UV-vis spectra of a chlorobenzene solution containing **1a** and [Ph<sub>3</sub>C][BF<sub>4</sub>]. The spectra were collected during 1 min.



Figure S12. UV-vis spectrum of salt [Ph<sub>3</sub>C][BF<sub>4</sub>] in chlorobenzene.

#### **One-electron oxidation of IDipp by [NO][SbF6]:**



# Scheme S3.

[NO][SbF<sub>6</sub>] (6.8 mg, 0.026 mmol) was added to a chlorobenzene solution (3 ml) of IDipp (**1a**) (10 mg, 0.026 mmol) at room temperature. Immediately after the addition, the solution turned purple, suggesting the formation of [**1a**]<sup>+</sup> and nitric oxide (NO), while it became progressively yellowish over time. Kinetic analysis (Figure S13) of a freshly prepared reaction mixture revealed a first order decay ( $k_{obs} = 0.002 \text{ s}^{-1}$ ) of an absorption band centred at 560 nm, which we ascribe to [**1a**]<sup>+</sup>. The continuous absorption throughout almost the entire visible region observed at the end is in line with the presence of NO (see reference S3).



Figure S13. a) Evolution of the UV-vis spectra of 1a in PhCl immediately after the addition of  $[NO][SbF_6]$  (the time between the collection of each spectrum is 20 seconds). b) Absorbance at 560 nm over time. The dotted line represents the best fit to the first order kinetic model.

**N.B.:** UV-vis measurements of mixtures of **1a** and [Ph<sub>3</sub>C][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>], [Ph<sub>3</sub>C][BF<sub>4</sub>], or [NO][SbF<sub>6</sub>] show that the counter anion influences the UV-vis absorption of the radical cation [**1a**]<sup>++</sup> ( $\lambda$  = 591 nm with B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub><sup>-</sup>;  $\lambda$  = 556 nm with BF<sub>4</sub><sup>-</sup>;  $\lambda$  = 560 with SbF<sub>6</sub><sup>-</sup>). This influence is probably due to week interactions between the radical cation [**1a**]<sup>++</sup> and the respective anion.

# **Reaction of IDipp with [NO][SbF6] in toluene:**



# Scheme S4.

Toluene (3 mL) was added to a mixture of IDipp (1a) (50 mg, 0.129 mmol) and [NO][SbF<sub>6</sub>] (34 mg, 0.129 mmol) at room temperature. The color of solution changed to purple, and then to pale-yellow. The resulting suspension was stirred for overnight. After that, the solvent was removed under vacuum, and the residue was used for NMR spectroscopy without purification. <sup>1</sup>H NMR spectroscopy indicated that the formation of the imidazolium salt **5** as main product (see Figure S14).

<sup>1</sup>H NMR (400 MHz, 298 K, [D<sub>2</sub>]dichloromethane):  $\delta = 1.22$  (d, <sup>3</sup>*J*(<sup>1</sup>H-<sup>1</sup>H) = 6.8 Hz, 12H, CH(C<u>H</u><sub>3</sub>)<sub>2</sub>), 1.30 (d, <sup>3</sup>*J*(<sup>1</sup>H-<sup>1</sup>H) = 6.8 Hz, 12H, CH(C<u>H</u><sub>3</sub>)<sub>2</sub>), 2.40 (sept., <sup>3</sup>*J*(<sup>1</sup>H-<sup>1</sup>H) = 6.8 Hz, 4H, C<u>H</u>(CH<sub>3</sub>)<sub>2</sub>), 7.43 (d, <sup>3</sup>*J*(<sup>1</sup>H-<sup>1</sup>H) = 7.9 Hz, 4H, *m*-Dipp), 7.65 (t, <sup>3</sup>*J*(<sup>1</sup>H-<sup>1</sup>H) = 7.9 Hz, 2H, *p*-Dipp), 7.70 (s, 2H, C<u>H</u>=CH), 8.44 (s, 1H, N-C<u>H</u>-N).



**Figure S14.** <sup>1</sup>H NMR (400 MHz, 298 K, [D<sub>2</sub>]dichloromethane) spectrum of the products obtained by reaction of IDipp (**1a**) with [NO][SbF<sub>6</sub>] in toluene at room temperature (#: unknown side products).

#### Reactions of [IDipp] with [CPh<sub>3</sub>][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] in the presence of THF:



#### Scheme S5.

A toluene/THF (1:1) solution (2 mL) of IDipp (1a) (50 mg, 0.129 mmol) was added slowly to a stirred toluene solution (2 mL) of  $[Ph_3C][B(C_6F_5)_4]$  (119 mg, 0.129 mmol) at room temperature. The color of solution changed from orange to purple, and then to brown. The resulting reaction mixture was stirred for overnight. After that, the solvent was removed under vacuum, and the residue was used for NMR spectroscopy without purification. The results of the NMR spectroscopic analysis indicated the formation of mixture of 2a (a peak at 4.76 ppm, see Figures S15a), 3a (a peak at 8.31 ppm) and Ph<sub>3</sub>CH (a peak at 5.57 ppm). The ratio of adduct 2a, 3a and Ph<sub>3</sub>CH is 0.37 : 1 : 1 (see Figure S15a).



**Figure S15a.** <sup>1</sup>H NMR (400 MHz, 298 K,  $[D_2]$ dichloromethane) spectrum of the products of the reaction between IDipp and  $[Ph_3C][B(C_6F_5)_4]$  in the presence of THF.

# Reaction of IDipp with [CPh<sub>3</sub>][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] in the presence of triphenyltin hydride:



# Scheme S6.

A toluene (4 mL) solution of Ph<sub>3</sub>SnH (45 mg, 0.128 mmol) was added to the mixture of [Ph<sub>3</sub>C][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] (59.5 mg, 0.064 mmol) and IDipp (**1a**) (25 mg, 0.064 mmol) at room temperature. The color of solution changed from orange to purple, and then to light-yellow. The reaction mixture was stirred for another 30 min. The solvent was removed under vacuum, and the residue was analysed by NMR spectroscopy. The NMR spectra indicated the formation of a mixture of **2a** (a peak at 4.76 ppm, see Figures S16a), **3a** (a peak at 8.31 ppm) and Ph<sub>3</sub>CH (a peak at 5.57 ppm), along with the by-product Ph<sub>3</sub>SnSnPh<sub>3</sub> (a peak at 131.1 ppm in the <sup>119</sup>Sn NMR spectrum , see Figure S16b). The yield of the imidazolium salt **3a** is 42% (yield of **3a** was determined by using ClCH<sub>2</sub>CH<sub>2</sub>Cl (0.063 mmol) as internal standard, see Figure S16a).

# NMR data of Ph<sub>3</sub>SnSnPh<sub>3</sub>:

<sup>1</sup>H NMR (400 MHz, 298 K, [D<sub>2</sub>]dichloromethane):  $\delta = 7.42$  (m, 12H, <u>Ph</u><sub>3</sub>SnSnPh<sub>3</sub>), 7.61 (m, 18H, <u>Ph</u><sub>3</sub>SnSnPh<sub>3</sub>).

<sup>119</sup>Sn NMR (149.1 MHz, 298 K, [D<sub>2</sub>]dichloromethane):  $\delta = 131.1$  (s, Ph<sub>3</sub>SnPh<sub>3</sub>).

# NMR data of Ph<sub>3</sub>CH:

<sup>1</sup>H NMR (400 MHz, 298 K, [D<sub>2</sub>]dichloromethane):  $\delta = 5.57$  (s, 12H, Ph<sub>3</sub>C<u>H</u>), 7.15 (m, 6H, *o*-<u>Ph</u><sub>3</sub>CH), 7.23 (m, 3H, *p*-<u>Ph</u><sub>3</sub>CH), 7.31 (m, 6H, *m*-<u>Ph</u><sub>3</sub>CH).



**Figure S16a.** <sup>1</sup>H NMR (400 MHz, 298 K,  $[D_2]$  dichloromethane) spectrum of the products of the reaction between IDipp and  $[Ph_3C][B(C_6F_5)_4]$  in the presence of  $Ph_3SnH$  (#: unknown side product. ClCH<sub>2</sub>CH<sub>2</sub>Cl (0.063 mmol) was added to the CD<sub>2</sub>Cl<sub>2</sub> solution as internal standard).



**Figure S16b.** <sup>119</sup>Sn NMR (149 MHz, 298 K,  $[D_2]$ dichloromethane) spectrum of the products of the reaction between IDipp and  $[Ph_3C][B(C_6F_5)_4]$  in the presence of  $Ph_3SnH$ .



**Figure S16c.** <sup>1</sup>H NMR (400 MHz, 298 K,  $[D_2]$  dichloromethane) spectrum of triphenylmethane (isolated from the reaction mixture by extraction with *n*-pentane).

Synthesis of imidazolium salt 3a:



### Scheme S7.

Dichloromethane (2 ml) was added to a mixture of 1,3-bis(2,6-diisopropylphenyl)imidazolium chloride (50 mg, 0.120 mmol) and potassium tetrakis(pentafluorophenyl)borate (85 mg, 0.120 mmol) at room temperature. The reaction mixture was stirred for overnight. The resulting mixture was filtered by using a PTFE syringe filter to remove KCl. The solvent of the filtrate was removed under reduced pressure, and the remaining colorless solid was used for NMR spectroscopy without purification. On the basis of the analysis of the NMR spectra, the yield of imidazolium salt **3a** is almost quantitative. Colorless crystals of salt **3a**, suitable for XRD analysis, were obtained from DCM at room temperature.

<sup>1</sup>H NMR (400 MHz, 298 K, [D<sub>2</sub>]dichloromethane):  $\delta = 1.22$  (d, <sup>3</sup> $J(^{1}H^{-1}H) = 6.8$  Hz, 12H, CH(C<u>H</u><sub>3</sub>)<sub>2</sub>), 1.30 (d, <sup>3</sup> $J(^{1}H^{-1}H) = 6.8$  Hz, 12H, CH(C<u>H</u><sub>3</sub>)<sub>2</sub>), 2.37 (sept., <sup>3</sup> $J(^{1}H^{-1}H) = 6.8$  Hz, 4H, C<u>H</u>(CH<sub>3</sub>)<sub>2</sub>), 7.45 (d, <sup>3</sup> $J(^{1}H^{-1}H) = 7.9$  Hz, 4H, *m*-Dipp), 7.62 (s, 2H, C<u>H</u>=CH), 7.67 (t, <sup>3</sup> $J(^{1}H^{-1}H) = 7.9$  Hz, 2H, *p*-Dipp), 8.31 (s, 1H, N-C<u>H</u>-N).

<sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, 298 K, [D<sub>2</sub>]dichloromethane): δ = 23.8, 24.6 (CH(<u>C</u>H<sub>3</sub>)<sub>2</sub>), 29.7 (<u>C</u>H(CH<sub>3</sub>)<sub>2</sub>), 125.6 (*m*-Dipp), 126.3 (<u>C</u>H=CH), 129.4 (*ipso*-Dipp), 129.4 (*p*-Dipp), 136.7 (dm, <sup>1</sup>*J*(<sup>13</sup>C-<sup>19</sup>F) = 246 Hz, *m*-<u>C</u>-C<sub>6</sub>F<sub>5</sub>), 136.9 (N<u>C</u>N), 138.6 (dm, <sup>1</sup>*J*(<sup>13</sup>C-<sup>19</sup>F) = 244 Hz, *p*-<u>C</u>-C<sub>6</sub>F<sub>5</sub>), 145.3 (*o*-Dipp), 148.4 (dm, <sup>1</sup>*J*(<sup>13</sup>C-<sup>19</sup>F) = 244 Hz, *o*-<u>C</u>-C<sub>6</sub>F<sub>5</sub>).

<sup>11</sup>B{<sup>1</sup>H} NMR (128 MHz, 298 K, [D<sub>2</sub>]dichloromethane):  $\delta = -16.6 (\underline{B}(C_6F_5)_4)$ .

<sup>19</sup>F{<sup>1</sup>H} NMR (377 MHz, 298 K, [D<sub>2</sub>]dichloromethane):  $\delta = -133.0$  (dm, *o*-C<u>F</u>), -163.7 (t, *p*-C<u>F</u>, <sup>3</sup>*J*(<sup>19</sup>F-<sup>19</sup>F) = 21 Hz), -167.6 (t, *m*-C<u>F</u>, <sup>3</sup>*J*(<sup>19</sup>F-<sup>19</sup>F) = 18 Hz).

HRMS (ESI/QTOF) m/z: [M]<sup>+</sup> Calcd for C<sub>27</sub>H<sub>37</sub>N<sub>2</sub><sup>+</sup> 389.2951; Found 389.2949.

HRMS (ESI/QTOF) m/z: [M]<sup>-</sup> Calcd for C<sub>24</sub>BF<sub>20</sub><sup>-</sup> 678.9779; Found 678.9778.



Figure S17a. <sup>1</sup>H NMR (400 MHz, 298 K, [D<sub>2</sub>]dichloromethane) spectrum of **3a**.



Figure S17b. <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, 298 K, [D<sub>2</sub>]dichloromethane) spectrum of **3a**.



Figure S17c. <sup>11</sup>B{<sup>1</sup>H} NMR (128 MHz, 298 K, [D<sub>2</sub>]dichloromethane) spectrum of **3a**.



Figure S17d. <sup>19</sup>F{<sup>1</sup>H} NMR (377 MHz, 298 K, [D<sub>2</sub>]dichloromethane) spectrum of **3a**.

Reaction of ItBu with [Ph<sub>3</sub>C][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] at -40 °C:



#### Scheme S8.

A toluene solution (2 mL) of I*t*Bu (**1b**) (256 mg, 0.278 mmol) was added slowly to a stirred toluene solution (2 mL) of  $[Ph_3C][B(C_6F_5)_4]$  (50 mg, 0.278 mmol) at -40 °C. The color of solution changed from orange to purple, and then to yellow. The mixture was stirred for another 1 h. After that, the solvent was removed under vacuum, and the residue was washed three-times with *n*-pentane (3 x 4 mL). The resulting yellow solid was dried under vacuum (Yield: 297 mg, 97%).

# NMR data of 2b (see reference S4):

<sup>1</sup>H NMR (400 MHz, 298 K, [D<sub>2</sub>]dichloromethane):  $\delta = 1.74$  (s, 9H, *t*Bu<u>H</u>), 1.78 (s, 9H, *t*Bu<u>H</u>), 5.76 (d of d, <sup>3</sup>*J*(<sup>1</sup>H-<sup>1</sup>H) = 3.0 Hz, 10.0 Hz, 2H, C<u>H</u>=CH), 5.87 (m, 1H, I*t*BuC<u>H</u>), 6.78 (d of d, <sup>3</sup>*J*(<sup>1</sup>H-<sup>1</sup>H) = 3.0 Hz, 10.0 Hz, 2H, C<u>H</u>=CH), 7.20 (m, 4H, *o*-C<u>Ph<sub>2</sub></u>), 7.36 (m, 6H, *m*, *p*-C<u>Ph<sub>2</sub></u>), 7.42 (d, <sup>3</sup>*J*(<sup>1</sup>H-<sup>1</sup>H) = 34.0 Hz, 1H, N-C<u>H</u>=CH), 7.44 (d, <sup>3</sup>*J*(<sup>1</sup>H-<sup>1</sup>H) = 34.0 Hz, 1H, N-C<u>H</u>=CH).



Figure S18. <sup>1</sup>H NMR (400 MHz, 298 K, [D<sub>2</sub>]dichloromethane) spectrum of 2b.

# Reaction of ItBu with [Ph<sub>3</sub>C][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] in the presence of THF:



#### Scheme S9.

A toluene/THF (1:1) solution (2 mL) of ItBu (1b) (25 mg, 0.139 mmol) was added slowly to a stirred toluene solution (2 mL) of  $[Ph_3C][B(C_6F_5)_4]$  (128 mg, 0.139 mmol) at room temperature. The color of solution changed from orange to purple, and then to brown. The resulting mixture was stirred for overnight. After that, the solvent was removed under vacuum, and the residue was used for NMR spectroscopy without purification. <sup>1</sup>H NMR spectroscopy indicated that the formation of **2b**, **3b** and Ph<sub>3</sub>CH in a ratio of 0.26 : 1 : 1 (see Figure S19).



**Figure S19.** <sup>1</sup>H NMR (400 MHz, 298 K,  $[D_2]$  dichloromethane) spectrum of the products of the reaction between I*t*Bu and  $[Ph_3C][B(C_6F_5)_4]$  in the presence of THF.

Reaction of ItBu with [CPh<sub>3</sub>][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] in the presence of triphenyltin hydride:



# Scheme S10.

A toluene (2 mL) solution of Ph<sub>3</sub>SnH (195 mg, 0.556 mmol) was added to a mixture of [Ph<sub>3</sub>C][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] (256 mg, 0.278 mmol) and *It*Bu (**1b**) (50 mg, 0.278 mmol) at room temperature. The color of solution changed from orange to purple and then to light-yellow. The reaction mixture was stirred for another 30 min. The resulting solution separated as three layers. The upper two phases and the lower oily phase were allowed to separate. The solvent of upper two phases was removed under vacuum, and the results of an NMR spectroscopic analysis indicated the formation of Ph<sub>3</sub>SnSnPh<sub>3</sub> (a peak at 131.1 ppm in <sup>119</sup>Sn NMR spectrum, see Figure S20g) and Ph<sub>3</sub>CH (a peak at 5.57 ppm, see Figure S20f). The separated lower colourless solid was identified as the imidazolium salt **3b** (a peak at 8.16 ppm, see Figure S20a), which was formed in 87% yield (yield of **3b** was determined by using ClCH<sub>2</sub>CH<sub>2</sub>Cl (0.063 mmol) as internal standard, see Figure S20a).

#### NMR data of 3b:

<sup>1</sup>H NMR (400 MHz, 298 K, [D<sub>2</sub>]dichloromethane):  $\delta = 1.65$  (s, 18H, *t*Bu), 7.44 (s, 2H, C<u>H</u>=CH), 8.16 (s, 1H, N-C<u>H</u>-N).

<sup>13</sup>C {<sup>1</sup>H} NMR (101 MHz, 298 K, [D<sub>2</sub>]dichloromethane):  $\delta = 29.7$  (*t*Bu), 61.5 (*t*Bu), 121.0 (<u>C</u>H=CH), 129.4 (N-<u>C</u>H-N), 124.8 (br, *ipso*-<u>C</u>-C<sub>6</sub>F<sub>5</sub>), 136.7 (dm, <sup>1</sup>J(<sup>13</sup>C-<sup>19</sup>F) = 246 Hz, *m*-<u>C</u>-C<sub>6</sub>F<sub>5</sub>), 138.7 (dm, <sup>1</sup>J(<sup>13</sup>C-<sup>19</sup>F) = 244 Hz, *p*-<u>C</u>-C<sub>6</sub>F<sub>5</sub>), 148.6 (dm, <sup>1</sup>J(<sup>13</sup>C-<sup>19</sup>F) = 242 Hz, *o*-<u>C</u>-C<sub>6</sub>F<sub>5</sub>).

<sup>11</sup>B{<sup>1</sup>H} NMR (128 MHz, 298 K, [D<sub>2</sub>]dichloromethane):  $\delta = -16.6 (\underline{B}(C_6F_5)_4)$ .

<sup>19</sup>F{<sup>1</sup>H} NMR (377 MHz, 298 K, [D<sub>2</sub>]dichloromethane):  $\delta = -133.0 \text{ (dm, } o\text{-C}\underline{F}\text{)}, -163.7 \text{ (t, } p\text{-C}\underline{F}\text{, } {}^{3}J({}^{19}\text{F}\text{-}{}^{19}\text{F}\text{)} = 21 \text{ Hz}\text{)}, -167.6 \text{ (t, } m\text{-C}\underline{F}\text{, } {}^{3}J({}^{19}\text{F}\text{-}{}^{19}\text{F}\text{)} = 18 \text{ Hz}\text{)}.$ 

HRMS (ESI/QTOF) m/z:  $[M]^+$  Calcd for  $C_{11}H_{21}N_2^+$  181.1699; Found 181.1699.



**Figure S20a.** <sup>1</sup>H NMR (400 MHz, 298 K,  $[D_2]$ dichloromethane) spectrum of **3b** (#:impurities, ClCH<sub>2</sub>CH<sub>2</sub>Cl (0.063 mmol) was added to the CD<sub>2</sub>Cl<sub>2</sub> solution as internal standard).



Figure S20b. <sup>1</sup>H NMR (400 MHz, 298 K, [D<sub>2</sub>]dichloromethane) spectrum of 3b (#: impurities).



Figure S20c.  $^{13}\mathrm{C}\{^{1}\mathrm{H}\}$  NMR (101 MHz, 298 K, [D<sub>2</sub>]dichloromethane) spectrum of 3b.



Figure S20d. <sup>11</sup>B{<sup>1</sup>H} NMR (128 MHz, 298 K, [D<sub>2</sub>]dichloromethane) spectrum of **3b**.



Figure S20e.  ${}^{19}F{}^{1}H$  NMR (377 MHz, 298 K, [D<sub>2</sub>]dichloromethane) spectrum of **3b**.



**Figure 20f.** <sup>1</sup>H NMR (400 MHz, 298 K, [D<sub>2</sub>]dichloromethane) spectrum of the mixture of compounds Ph<sub>3</sub>SnSnPh<sub>3</sub> and Ph<sub>3</sub>CH.



Figure S20g. <sup>119</sup>Sn NMR (149 MHz, 298 K, [D<sub>2</sub>]dichloromethane) spectrum of Ph<sub>3</sub>SnSnPh<sub>3</sub>.

# Reaction of IMes with [Ph<sub>3</sub>C][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] at -40 °C:



# Scheme S11.

A toluene solution (2 mL) of IMes **1c** (50 mg, 0.164 mmol) was added slowly to a stirred toluene solution (2 mL) of  $[Ph_3C][B(C_6F_5)_4]$  (152 mg, 0.164 mmol) at -40 °C. The color of solution changed from orange to purple, and then to yellow. After that, the solvent was removed under vacuum, and the residue was used for NMR spectroscopy without purification. <sup>1</sup>H NMR spectroscopy indicated that the formation of **2c**, **3c** and **4** in a ratio of 1.74 : 1 : 27.12 (see Figure S21a). Adduct **4** was isolated by crystallization from DCM/*n*-hexane (1:1) (Yield: 20 mg, 10%).

# NMR data of 4:

<sup>1</sup>H NMR (400 MHz, 298 K, [D<sub>2</sub>]dichloromethane):  $\delta = 1.94$  (s, 12H, *o*-<u>Me</u>-Mes), 2.16 (s, 6H, *p*-<u>Me</u>-Mes), 6.58 (s, 4H, *m*-Mes), 7.00 (m, 12H, C<u>Ph<sub>3</sub></u>), 7.15 (m, 3H, C<u>Ph<sub>3</sub></u>), 7.35 (s, 2H, C<u>H</u>=CH).

<sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, 298 K, [D<sub>2</sub>]dichloromethane): δ = 20.0 (*o*-<u>Me</u>-Mes), 20.7 (*p*-<u>Me</u>-Mes), 64.5 (<u>CPh<sub>3</sub></u>), 127.3 (<u>CH</u>=CH), 127.6, 128.6, 131.8, 138.8 (<u>CPh<sub>3</sub></u>), 130.6, 133.7, 135.0, 141.3 (Mes), ), 136.7 (dm, <sup>1</sup>*J*(<sup>13</sup>C-<sup>19</sup>F) = 244 Hz, *m*-<u>C</u>-C<sub>6</sub>F<sub>5</sub>), 138.7 (dm, <sup>1</sup>*J*(<sup>13</sup>C-<sup>19</sup>F) = 244 Hz, *p*-<u>C</u>-C<sub>6</sub>F<sub>5</sub>), 148.5 (dm, <sup>1</sup>*J*(<sup>13</sup>C-<sup>19</sup>F) = 244 Hz, *o*-<u>C</u>-C<sub>6</sub>F<sub>5</sub>), 150.8 (N-<u>C</u>-N).

<sup>11</sup>B{<sup>1</sup>H} NMR (128 MHz, 298 K, [D<sub>2</sub>]dichloromethane):  $\delta = -16.6 (\underline{B}(C_6F_5)_4)$ .

<sup>19</sup>F{<sup>1</sup>H} NMR (377 MHz, 298.0 K, [D<sub>2</sub>]dichloromethane):  $\delta = -133.1$  (dm, *o*-C<u>F</u>), -163.7 (t, *p*-C<u>F</u>, <sup>3</sup>*J*(<sup>19</sup>F-<sup>19</sup>F) = 21 Hz), -167.5 (t, *m*-C<u>F</u>, <sup>3</sup>*J*(<sup>19</sup>F-<sup>19</sup>F) = 18 Hz).

HRMS (ESI/QTOF) m/z:  $[M]^+$  Calcd for  $C_{40}H_{39}N_2^+$  547.3108; Found 547.3110.

HRMS (ESI/QTOF) m/z: [M]<sup>-</sup> Calcd for C<sub>24</sub>BF<sub>20</sub><sup>-</sup> 678.9779; Found 678.9974.



**Figure S21a.** <sup>1</sup>H NMR (400 MHz, 298 K,  $[D_2]$  dichloromethane) spectrum of the products formed by reaction of IMes (**1c**) with  $[Ph_3C][B(C_6F_5)_4]$  at room temperature.



Figure S21b. <sup>1</sup>H NMR (400 MHz, 298.0 K, [D<sub>2</sub>]dichloromethane) spectrum of 4.



Figure S21c.  ${}^{13}C{}^{1}H$  NMR (101 MHz, 298 K, [D<sub>2</sub>]dichloromethane) spectrum of 4.



Figure S21d. <sup>11</sup>B{<sup>1</sup>H} NMR (128 MHz, 298 K, [D<sub>2</sub>]dichloromethane) spectrum of 4.



Figure S21e.  ${}^{19}F{}^{1}H$  NMR (377 MHz, 298 K, [D<sub>2</sub>]dichloromethane) spectrum of 4.

Reaction of IMes with [CPh<sub>3</sub>][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] in the presence of THF:



### Scheme S12.

A toluene/THF (1:1) solution (2 mL) of IMes (1c) (25 mg, 0.082 mmol) was added slowly to a stirred toluene solution (2 mL) of  $[Ph_3C][B(C_6F_5)_4]$  (76 mg, 0.082 mmol) at room temperature. The color of solution changed from orange to purple, and then to light-yellow. The resulting reaction mixture was stirred for overnight. After that, the solvent was removed under vacuum, and the residue was used for NMR spectroscopy without purification. <sup>1</sup>H NMR spectroscopy indicated the formation of **3c** and Ph<sub>3</sub>CH in a yield of 63% (see Figure S22a). After washing with *n*-pentane, the remaining colorless solid was identified as pure **3c** (see Figure S22b).

# NMR data of 3c:

<sup>1</sup>H NMR (400 MHz, 298 K, [D<sub>2</sub>]dichloromethane):  $\delta = 2.12$  (s, 12H, *o*-<u>Me</u>-Mes), 2.38 (s, 6H, *p*-<u>Me</u>-Mes), 7.13 (s, *m*-Mes), 7.55 (s, 2H, C<u>H</u>=CH), 8.26 (s, 1H, N-C<u>H</u>-N).

<sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, 298 K, [D<sub>2</sub>]dichloromethane):  $\delta = 17.3$  (*o*-<u>Me</u>-Mes), 21.2 (*p*-<u>Me</u>-Mes), 123.6 (br, *ipso*-<u>C</u>-C<sub>6</sub>F<sub>5</sub>), 125.6 (<u>C</u>H=CH), 130.2 (*p*-Mes), 130.6 (*m*-Mes), 134.3 (*ipso*-Mes), 136.0 (N-<u>C</u>-N), 136.7 (dm, <sup>1</sup>J(<sup>13</sup>C-<sup>19</sup>F) = 244 Hz, *m*-<u>C</u>-C<sub>6</sub>F<sub>5</sub>), 138.7 (dm, <sup>1</sup>J(<sup>13</sup>C-<sup>19</sup>F) = 244 Hz, *p*-<u>C</u>-C<sub>6</sub>F<sub>5</sub>), 143.1 (*o*-Mes), 148.5 (dm, <sup>1</sup>J(<sup>13</sup>C-<sup>19</sup>F) = 242 Hz, *o*-<u>C</u>-C<sub>6</sub>F<sub>5</sub>).

<sup>11</sup>B{<sup>1</sup>H} NMR (128 MHz, 298 K, [D<sub>2</sub>]dichloromethane):  $\delta = -16.6 (\underline{B}(C_6F_5)_4)$ .

<sup>19</sup>F{<sup>1</sup>H} NMR (377 MHz, 298 K, [D<sub>2</sub>]dichloromethane):  $\delta = -132.9$  (dm, *o*-C<u>F</u>), -163.5 (t, *p*-C<u>F</u>, <sup>3</sup>*J*(<sup>19</sup>F-<sup>19</sup>F) = 21 Hz), -167.4 (t, *m*-C<u>F</u>, <sup>3</sup>*J*(<sup>19</sup>F-<sup>19</sup>F) = 18 Hz).

HRMS (ESI/QTOF) m/z:  $[M]^+$  Calcd for  $C_{21}H_{25}N_2^+$  305.2012; Found 305.2010.



**Figure S22a.** <sup>1</sup>H NMR (400 MHz, 298 K, [D<sub>2</sub>]dichloromethane) spectrum of the reaction mixture (#: impurities).



Figure S22b. <sup>1</sup>H NMR (400 MHz, 298 K, [D<sub>2</sub>]dichloromethane) spectrum of 3c.



Figure S22c. <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, 298 K, [D<sub>2</sub>]dichloromethane) spectrum of 3c.



Figure S22d. <sup>11</sup>B{<sup>1</sup>H} NMR (128 MHz, 298 K, [D<sub>2</sub>]dichloromethane) spectrum of 3c.



Figure S22e.  ${}^{19}F{}^{1}H$  NMR (377 MHz, 298 K, [D<sub>2</sub>]dichloromethane) spectrum of 3c.

#### **Crystallographic Analyses**

Bragg-intensities of **2a**, **3a**, **3b** and **4** were collected at 140 K using Cu  $K\alpha$  radiation. A Rigaku SuperNova dual system diffractometer with an Atlas S2 CCD detector was used for compounds **2a**, **3a** and **4**, and one equipped with an Atlas CCD detector for compound **3b**. The datasets were reduced and corrected for absorption, with the help of a set of faces enclosing the crystals as snugly as possible, with the latest available version of *CrysAlis<sup>Pro.S5</sup>* The solutions and refinements of the structures were performed by the latest available version of *ShelXT* <sup>S6</sup> and *ShelXL.*<sup>S7</sup> All non-hydrogen atoms were refined anisotropically using full-matrix least-squares based on  $|F|^2$ . The hydrogen atoms were placed at calculated positions by means of the "riding" model in which each H-atom was assigned a fixed isotropic displacement parameter with a value equal to 1.2  $U_{eq}$  of its parent C-atom (1.5  $U_{eq}$  for the methyl groups). Crystallographic and refinement data are summarized in Table S1. Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre and correspond to the following codes: **2a** (1980460), **3a** (1980461), **3b** (1980595) and **4** (1980462). These data can be obtained free of charge via www.ccdc.cam.ac.uk/data\_request/cif, or by emailing data\_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

In the structure 3a, one of C<sub>6</sub>F<sub>5</sub> rings is disordered over two orientations each, found in a difference map. These were anisotropically refined imposing distance and similarity restraints (SADI, AFIX; FLAT and SIMU) for the least-squares refinement, yielding site occupancies of 0.679(7)/0.321(7).

Compound	2a	3a	3b	4
Empirical formula	$C_{71}H_{53}BCl_2F_{20}N_2$	$C_{52}H_{39}BCl_2F_{20}N_2$	$C_{35}H_{21}BF_{20}N_2$	$C_{64}H_{39}BF_{20}N_2$
Temperature (K)	140(10)	140(10)	140(10)	140(10)
Formula weight	1395.86	1153.56	860.35	1226.78
Wavelength (Å)	1.54184	1.54184	1.54184	1.54184
Crystal system	triclinic	triclinic	monoclinic	orthorhombic
Space group	P1	PĪ	<i>P2</i> <sub>1</sub>	Pbca
<i>a</i> (Å)	13.2446(5)	12.4784(2)	8.40488(13)	18.0482(3)
<i>b</i> (Å)	13.7731(5)	12.6328(3)	18.0272(3)	18.05071(19)
<i>c</i> (Å)	20.2266(8)	17.6483(5)	11.08430(15)	34.8012(5)
$\alpha$ (deg)	94.923(3)	69.366(2)	90	90
$\beta$ (deg)	102.959(3)	84.7909(18)	91.4773(5)	90
$\gamma(\text{deg})$	114.918(4)	18.9069(16)	90	90
$V(\text{\AA}^3)$	3192.5(2)	2554.11(11)	1678.89(4)	11337.6(3)
Ζ	2	2	2	8
$D_{ m calcd} ({ m Mg} /{ m m}^3)$	1.452	1.500	1.702	1.437
$\mu (\text{mm}^{-1})$	1.832	2.156	1.609	1.138
F(000)	1424	1168	860	4976
$\theta$ range (°)	3.615 ~ 72.742	2.676~72.740	4.684 ~ 76.459	3.528 ~ 76.243
Ref. collected	22810	18050	16823	127435
Independent reflections	12281 ( $R_{\rm int} = 0.0282$ )	9870 ( $R_{int} = 0.0106$ )	$6954 \ (R_{\rm int} = 0.0184)$	11828 ( $R_{\rm int} = 0.0448$ )
Completeness to $\theta$ (°)	72.74 (99.6 %)	72.74 (100 %)	67.68 (99.8 %)	76.24 (100 %)
Goodness-of-fit on $ F ^2$	1.025	1.022	1.065	1.046
Final <i>R</i> indices $[I > 2\sigma(I)]^a$	$R_1 = 0.0433$	$R_1 = 0.0520$	$R_1 = 0.0280$	$R_1 = 0.0402$
	$wR_2 = 0.1097$	$wR_2 = 0.1491$	$wR_2 = 0.0772$	$wR_2 = 0.1068$
R indices (all data)	$R_1 = 0.0542$	$R_1 = 0.0540$	$R_1 = 0.0284$	$R_1 = 0.1109$
	$wR_2 = 0.1185$	$wR_2 = 0.1510$	$wR_2 = 0.0774$	$wR_2 = 0.0453$
$\Delta \rho_{\rm max, min}  ({\rm e}/{\rm \AA}^3)$	0.335, -0.494	0.930, -0.949	0.250, -0.201	0.277, -0.202
CCDC code	1980460	1980461	1980595	1980462

 Table S1. Crystal data and structure refinement for 2a, 3a, 3b and 4.

<sup>*a*</sup>  $R_I = ||Fo| - |Fc||/|Fo|, wR_2 = [\Sigma w (F_o^2 - F_c^2)^2 / \Sigma w (F_o^2)^2]^{1/2}$ 



**Figure S23.** Molecular structure of **2a** in the crystal. Hydrogen atoms, except H4, and the  $[B(C_6F_5)_4]^-$  anion are omitted for clarity. Thermal ellipsoids are shown at the 50% probability level. Selected bond lengths [pm]: N1–C1 134.3(2), N2–C1 134.0(2), C1–C4 151.2(2), C4–C5 150.1(3), C4–C9 150.5(2), C5–C6 133.5(3), C6–C7 146.4(2), C7–C8 145.7(3), C8–C9 133.7(3), C7–C10 136.0(3).



**Figure S24.** Molecular structure of **3a** in the crystal. Hydrogen atoms, except H1, and the  $[B(C_6F_5)_4]^-$  anion are omitted for clarity. Thermal ellipsoids are shown at the 50% probability level. Selected bond lengths [pm]: N1–C1 133.1(2), N2–C1 133.2(2), C1–H1 0.95.



**Figure S25.** Molecular structure of **3b** in the crystal. Hydrogen atoms, except H1, and the  $[B(C_6F_5)_4]^-$  anion are omitted for clarity. Thermal ellipsoids are shown at the 50% probability level. Selected bond lengths [pm]: N1–C1 132.9(3), N2–C1 132.8(3), C1–H1 0.95.



**Figure S26.** Molecular structure of **4** in the crystal. Hydrogen atoms and the  $[B(C_6F_5)_4]^-$  anion are omitted for clarity. Thermal ellipsoids are shown at the 50% probability level. Selected bond lengths [pm]: N1–C1 135.2(2), N2–C1 137.0(2), C1–C22 153.8(2).

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